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"Equilibria in solution" : 2,2,8,8-Tetrakishydroxymethyl-3, 7-diaza-1, 5,9 -nonanetriol and 2,2,8,8-Tetramethyl-3, 7-diaza-5-nonaneol with copper (II)

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"EQUILIBRIA IN SOLUTION"

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by

Ronald Weston Davis

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Approved By: Wm E. Trout Jr.
W. Allan Powell
J. Kenneth Pierce
Jackson J. Taylor
M. M. Fleming

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ABSTRACT

The chelating agents, 2,2,8,8-Tetrakishydroxymethyl-3,7-diaza-1,5,9-nonanetriol ("Disec") and 2,2,8,8-Tetramethyl-3,7-diaza-5-nonaneol ("Symaminol") were prepared and investigated with respect to their Basicity and Stability Constants.

The compound, "Disec," investigated in earlier work was again studied using more precise and controlled conditions of temperature ($30.000 \pm 0.002^{\circ}C$), measured pH readings and volume readings.

The compound, "Symaminol," was prepared in the laboratory and studied in the same manner as "Disec." Examination of the literature yielded no evidence of "Symaminol" having been previously investigated.

By means of a digital computer, the data was correlated in a manner as to investigate the Basicity Constant and Stability Constant curves of the two compounds.

Some understanding of the values and limits of the method to determine such constants were evaluated.

I

INTRODUCTION

The determination of equilibrium constants is of primary importance in the study of chelate approach to the accumulation of data which should lead to a more comprehensive understanding of chelates and the relationships which goven their formation and structure.

At the beginning of the Twentieth Century, Bodländer, Luther, Abegg and their co-workers were already studying complex equilibria, and several of the present-day experimental methods were introduced at that time. In most cases, these investigators used a great excess of ligand and usually had only one complex to take into consideration[1] but Morse[2] and Sherill[3] had proved the existence of several complexes with mercury(II) chloride system. It was Bjerrum[4] who was the first to emphasize that complex formation was generally a stepwise process.

A number of factors offer serious limitations to the methods available. The reaction must come to equilibrium in a reasonable time and the measurements should not appreciably disturb the equilibrium. Many chelates are insoluble in water. Although they are in many cases soluble in non-aqueous solvents, our knowledge of the nature of ions, particularly metal ions, in such solvents is even less satisfactory than it is for water.

The structure of the chelating agents is often quite complicated. They are usually ionic and often contain dipolar ions, and many contain one or more dipolar ions and one or more simple ionic groups in the same molecule. Our knowledge of the

behavior of such structures in aqueous solution is inadequate to allow evaluation of their activity even when very dilute solutions are used. Qualitatively, we know that deviations from ideal behavior of such substances is even great in solutions of the order of 10^{-3} Molar. Measurements of stability constants involving such substances are usually carried out by "swamping" the chelating agent with simple ions to give a solution of known ionic strength. Thus, the activity coefficient, though unknown, is maintained constant, and "apparent" formation constants may be calculated.

$$K_c = \frac{m_{Mke_x}}{m_M \cdot m_{ke}^x}$$

$$K_{eq} = K_c \cdot \frac{\gamma_{Mke_x}}{\gamma_M \ \gamma_{ke}^x}$$

where,

K_c = apparent equilibrium constant

m = molar concentration

γ = activity coefficient

K_{eq} = actual equilibrium constant.

In practice, K_c is usually determined. This may be converted to K_{eq}, the thermodynamic equilibrium or formation constant, by determining K_c for various values of m and extrapolating to infinite dilution, for which all values of γ become equal to unity and $K_c = K_{eq}$.

The supporting or "swamping" electrolyte used should form only very weak complexes with the central metal ion and should be a very soluble salt. Since the perchlorate ion has a very slight tendency to form complexes, sodium perchlorate has been widely used as a supporting electrolyte. However, there is some evidence for the formation of perchlorate complexes with Iron(III) and Cerium(III).[5] Thus, in some cases, there is a certain degree of competition between the perchlorate ion and the ligand under study, but generally this competition is of minor importance.

Quantitative information is obtained by determining the stability or formation constants. The term stability refers to the degree of association that occurs in solution between two species in a state of equilibruim. Qualitatively, the greater the association, the greater the stability of the compound that results. Quantitatively, the magnitude of the equilibruim (stability or formation) constant for the association expresses the stability. This constant is expressed in powers of 10, usually a positive number, and thus is the inverse of the so-called instability constant frequently encountered in qualitative analysis.

A very important method in determining stability constants is to determine the pH of a solution potentiometrically. The pH of a solution is affected directly by chelate formation since most chelating agents can be regarded as Lewis acids or Lewis bases (an acid is an electron pair acceptor; a base is an electron pair donor). Thus, the pH of a solution is affected by the accepting or donating of a pair of electrons.

The most widely applicable method for determining equilibrium constants depend upon the fact that the potential of a reversible electrochemical cell is directly related to the activity of the ions involved in the cell reaction by the Nernst Equation,

$$E = E^{o} - \frac{RT}{nF} \ln \frac{(C)^{c}\ (D)^{d}}{(A)^{a}\ (B)^{b}} \quad . \ . \ .$$

in the general reaction,

$$aA + bB + \ . \ . \ . \rightleftharpoons cC + dD + \ . \ . \ .$$

The parenthesis, ( ), are used to express concentrations in units of moles per liter of solution (in this manuscript the typewriter is not capable of expressing concentration in the usual manner by use of brackets).

Harned[6] and associates used the potential of a cell to measure the dissociation constants of weak acids. The cell is represented by,

$$Pt \left| H_{2(g)} \right| HA,\ A^{-},\ H^{+},\ Cl^{-} \left| AgCl_{(s)} \right| Ag.$$

The dissociation constants in the above cell depend upon the activities of the hydrogen and chloride ions in the electrolyte solutions. The overall reaction of the cell is,

$$AgCl_{(s)} + 1/2\ H_{2(g)} \rightleftharpoons Ag + H^{+} + Cl^{-}$$

$$E^{o} = + 0.222 \text{ volts}$$

and according to the Nernst Equation, the potential of the cell is,

$$E = + 0.222 - 0.05915 \log (H^{+})(Cl^{-}).$$

If the activity of the chloride ion is held constant by using a fixed concentration of potassium chloride in the electrolyte, and the hydrogen ion results from the dissociation of a weak acid, then changing the amounts of weak acid and its salt present will vary (H^+) according to the equilibrium constant,

$$(H^+)(A^-) = K_a(HA)$$

and hence vary the potential of the cell.

One of the handiest and most widely used indicator electrodes is the glass electrode which is reversible to hydrogen ions.[7] Although the hydrogen gas electrode is the primary standard for the electrode potential scale, it is easily upset by the presence of oxidizing agents or heavy metal ions in solution. Because the potential of the glass electrode arises by transfer of hydrogen ions through a thin glass membrane and not by an oxidation process, the glass electrode is insensitive to metal ions, oxidizing agents and the like; therefore, it can be used to measure hydrogen ion concentrations in practically any system. The glass electrode forms the basis of the "pH Meters" which have found wide application.

The application of the glass electrode is based upon the fact that two solutions, one in each side of a thin glass membrane, assume a potential difference which in the main depends only upon the hydrogen ion concentration of the solutions. Calling the potentials of the two solutions E_1 and E_2, and the corresponding hydrogen ion activities $(a_H)_1$ and $(a_H)_2$, the potential of the glass electrode will follow the thermodynamic formula,

$$E_1 - E_2 = \frac{RT}{F} \ln \frac{(a_H)_1}{(a_H)_2} \quad .$$

It is probably that no electrode is 100% reversible in its functioning, but if one uses a sufficiently thin glass membrane of the correct type of glass, the deviation of the above formula will usually be quite small. As shown by Mac and Dole[8], the best type of glass is a pure sodium calcium silicate of the composition: 72% SiO_2, 22% Na_2O and 6% CaO. Even the best electrodes have a small "asymmetry potential" (defined as the difference measured when $(a_H)_1 = (a_H)_2$) amounting to several millivolts which must be assumed to be caused by mechanical tension in the glass and/or by differences between the two glass surfaces due to the fact that only the outer surface of the glass membrane has been in direct contact with the flame.

Haugaard[9] has thoroughly investigated the reasons why the glass electrode deviates from the thermodynamic formula and finds that the asymmetry potential is pH-dependent and that the radius of curvature of the glass membrane also plays a part.

In glass electrode measurements, as in all measurements in systems of high electrical resistance, it is important that the measurements be made in a sufficiently dry atmosphere. When the measurements are made in humid air of 70-80% or even greater relative humidity, a layer of dampness will settle on all objects and give rise to stray currents on the surface of the glass electrode or in the potentiometer itself, thus making it impossible to obtain constant potentials. Difficulties of this type have been experienced by workers.

Working just a few degrees above room temperature helps considerably to lower the relative atmosphere humidity; besides a temperature increase will relatively improve the insulation by reducing the interior resistance of the glass electrode[10]. Under favorable conditions as opposed to unfavorable conditions, it is possible to measure with an accuracy ten times greater.

The glass electrode is used in conjunction with the calomel half-cell ($Hg\text{-}Hg_2Cl_2$) which is represented by,

$$Ag \left| AgCl_{(s)} \right| KCl,\ H^+ \left| \begin{matrix}\text{glass}\\ \text{membrane}\end{matrix} \right| \begin{matrix}\text{unknown}\\ \text{solution}\end{matrix} \left| \begin{matrix}\text{salt}\\ \text{bridge}\end{matrix} \right| KCl \left| Hg_2Cl_{2(s)} \right| Hg.$$

The potential of the calomel half-cell is fixed by the concentration of the KCl in the cell; the potential of the silver chloride is fixed by the concentration of the KCl; and the concentration of the hydrogen ion inside the glass membrane is fixed by the concentration of the H^+. Thus, the only variable is the hydrogen ion concentration in the unknown solution. The potential of this cell has been found experimentally to follow over a wide range of hydrogen ion concentrations according to the relation,

$$E = E^\circ + 0.05915 \log (H^+),$$

where E° depends not only on the standard potentials of the silver chloride and calomel electrodes, but also on an "asymmetry potential" which is characteristic of each particular glass membrane, and which varies with the previous history of the membrane. This means that the glass electrode is not an absolute measure of the hydrogen ion

concentration, as is the hydrogen gas electrode, but must be calibrated at regular intervals against a standard buffer solution of known hydrogen ion concentration.

The hydrogen ion concentration may be satisfactorily determined using the glass electrode system if the metal ion, M^{z+}, is an ion of a univalent or bivalent metal, although glass membranes appear to behave somewhat erratically in the presence of highly charged ions such as In^{3+} and Th^{4+}.

The mathematical development of the basicity and stability constants of di-amines-metal systems is summarized by Professor Schwarzenbach[11] and has been developed in detail by this worker as follows,

(M) = metal ion

(Z) = ligand

(H) = hydrogen

(MZ_i) = metal bound to ligand

(H_iZ) = hydrogen bound to ligand

i = interger, 1, 2 . . .

$(M)_t$ = total amount of metal ion present (bound and unbound)

$$(M)_t = (M) + (MZ) + MZ_2 \qquad \text{Eq. 1}$$

$(Z)_t$ = total amount of ligand present (bound and unbound)

$$(Z)_t = \alpha(Z) + (MZ) + 2(MZ_2) \qquad \text{Eq. 2}$$

where $\alpha(Z)$ = ligand not bound to metal

$$\alpha(Z) = (Z) + (HZ) + (H_2Z) \qquad \text{Eq. 3}$$

but $K^{H}_{HZ} = \frac{(HZ)}{(H)\ (Z)} = K_A$ Eq. 4

and

$\bar{K}^{H}_{H_2Z} = \frac{(H_2Z)}{(H)^2\ (Z)} = K_B$ Eq. 5

$K^{H}_{H_2Z} = \frac{(H_2Z)}{(H)\ (HZ)} = \frac{K_B}{K_A} = K_C = \frac{\bar{K}^{H}_{H_2Z}}{K^{H}_{HZ}}$ Eq. 6

therefore, substituting Eqs. 4 and 5 in Eq. 3, the expression, $\alpha(Z)$, becomes,

$\alpha = 1 + (H)\ K^{H}_{HZ} + (H)^2\ \bar{K}^{H}_{H_2Z}$ Eq. 7

$(H)_t$ = total amount of hydrogen-ion present (bound and unbound)

$(H)_t = (2\cdot(Z)_t - (NaOH) = (H) - (OH) + \beta(Z)$ Eq. 8

where $\beta(Z)$ = ligand bound to hydrogen

$\beta(Z) = (HZ) + 2(H_2Z)$ Eq. 9

therefore, substituting Eqs. 4 and 5 in Eq. 9, the expression, β becomes,

$\beta = (H)\ K^{H}_{HZ} + 2(H)^2\ \bar{K}^{H}_{H_2Z}$ Eq. 10

or

$\beta = (H)\ K^{H}_{HZ} + 2(H)^2\ K^{H}_{HZ} \cdot K^{H}_{H_2Z}$ Eq. 11

In the determination of basicity constants, the metal-ion is not present; only hydrogen is bound to the ligand, so the expression, $(Z)_t$, becomes,

$$(Z)_t = (Z) + \sum_{m} (HZ) + (H_2Z) \qquad \text{Eq. 12}$$

$$\text{ie. } (Z)_t = \sum_{j=o} (H_jZ) \qquad \text{Eq. 13}$$

$$(H)_t = (Z)_t\,(m-a) = (H) - (OH) + \sum_{j=1}^{m} (H_jZ) \qquad \text{Eq. 14}$$

where m = 2 hydrogen-ions per molecule of ligand and a = concentration of NaOH;

therefore,

$$(Z)_t \cdot g = (HZ) + 2(H_2Z) \qquad \text{Eq. 15}$$

where g = effective number of ligand molecules bound per metal-ion.

Substitution Eq. 15 in Eq. 12 the expression becomes,

$$g(\ (Z) + (HZ) + (H_2Z)\ ) = (HZ) + 2(H_2Z) \qquad \text{Eq. 16}$$

collecting terms,

$$g(Z) + g(HZ) + g(H_2Z) - (HZ) - 2(H_2Z) = 0 \qquad \text{Eq. 17}$$

rearranging so as to be factorable,

$$g(Z) + g(HZ) - (HZ) + g(H_2Z) - 2(H_2Z) = 0 \qquad \text{Eq. 18}$$

factoring,

$$g(Z) + (g-1)(HZ) + (g-2)(H_2Z) = 0 \qquad \text{Eq. 19}$$

from Eqs. 4, 5, and 6, it is seen that

$$(HZ) = K^{H}_{HZ}\,(H)(Z) \qquad \text{Eq. 20}$$

and

$$(H_2Z) = K^{H}_{H_2Z}\,(H)(HZ) \qquad \text{Eq. 21}$$

substituting (HZ) of Eq. 20 in Eq. 21

$$(H_2Z) = K^{H}_{H_2Z}\,(H)\;K^{H}_{HZ}\,(H)(Z) \qquad \text{Eq. 22}$$

which simplifies to,

$$(H_2Z) = K^H_{HZ} \cdot K^H_{H_2Z} (H)^2(Z) \qquad \text{Eq. 23}$$

but

$$K^H_{HZ} \cdot K^H_{H_2Z} = \bar{K}^H_{H_2Z} \qquad \text{Eq. 6}$$

therefore,

$$(H_2Z) = \bar{K}^H_{H_2Z} (H)^2(Z) \qquad \text{Eq. 24}$$

substituting Eqs. 20 and 21 in Eq. 19 the expression becomes,

$$g(Z) + (g-1)(H)(Z) K^H_{HZ} + (g-2)(H)^2 (Z) K^H_{HZ} \cdot K^H_{H_2Z} = 0 \qquad \text{Eq. 25}$$

factoring (Z), the expression becomes

$$g + (g-1)(H) K^H_{HZ} + (g-2)(H)^2 K^H_{HZ} \cdot K^H_{H_2Z} = 0 \qquad \text{Eq. 26}$$

but

$$K^H_{HZ} \cdot K^H_{H_2Z} = \bar{K}^H_{H_2Z} \qquad \text{Eq. 6}$$

$$g + (g-1)(H) K^H_{HZ} + (g-2)(H)^2 \bar{K}^H_{H_2Z} = 0 \qquad \text{Eq. 27}$$

rearranging, Eq. 27 becomes,

$$(g-1)(H) K^H_{HZ} + (g-2)(H)^2 \bar{K}^H_{H_2Z} = -g \qquad \text{Eq. 28}$$

For several points on the titration curves of the basicity plots, values of g and (H) are obtained which provide pairs of equations of the form, Eq. 28, which are readily solved by the use of determinants. Values for g_1 and g_2 may be found by substituting values of V_1 and V_2, and H_1 and H_2 in the following equations,

$$g_1 = 2 - \frac{V_1 N}{Z \cdot 100} + \frac{K_w - (H_1)^2}{H_1 \cdot Z \left(\frac{100}{100 + V_1}\right)} \qquad \text{Eq. 29}$$

$$g_2 = 2 - \frac{V_2 N}{Z \cdot 100} + \frac{K_w - (H_2)^2}{H_2 \cdot Z \left(\frac{100}{100 + V_2}\right)} \qquad \text{Eq. 30}$$

where K_w^{12} (30°C) = 1.471×10^{-14} (± 0.002)

V_1 and V_2 = ml of NaOH used

H_1 and H_2 = molarity of hydrogen-ions

N = normality of NaOH (0.1031 N)

Z = total molarity of ligand and

$\frac{100}{100 + V}$ = total concentration for volume (100 + V)

Eq. 28 takes on the following forms for the values of g and (H),

$$\underbrace{(g_1 - 1)(H) K_{HZ}^{H}}_{a} + \underbrace{(g_1 - 2)(H)^2 K_{H_2Z}^{H}}_{b} = \underbrace{-g_1}_{e} \qquad \text{Eq. 31}$$

$$\underbrace{(g_2 - 1)(H) K_{HZ}^{H}}_{c} + \underbrace{(g_2 - 2)(H)^2 K_{H_2Z}^{H}}_{d} = \underbrace{-g_2}_{f} \qquad \text{Eq. 32}$$

The equations have the form;

$$ax + by = e \qquad \text{Eq. 33}$$

$$cx + dy = f \qquad \text{Eq. 34}$$

where,

$a = (g_1-1)(H)$

$c = (g_2-1)(H)$

$b = (g_1-2)(H)^2$

$d = (g_2-2)(H)^2$

$e = -g_1$

$f = -g_2$

which has the solution,

$$x = \frac{de - bf}{ad - bc} \qquad \text{Eq. 35}$$

$$y = \frac{af - ce}{ad - bc} \qquad \text{Eq. 36}$$

the determinant $\begin{vmatrix} ab \\ cd \end{vmatrix}$ equals ad - bc

the solution of a determinant, if ad - bc $\neq 0$

can be written[13],

$$x = \frac{\begin{vmatrix} eb \\ fd \end{vmatrix}}{\begin{vmatrix} ab \\ cd \end{vmatrix}} \qquad y = \frac{\begin{vmatrix} ae \\ cf \end{vmatrix}}{\begin{vmatrix} ab \\ cd \end{vmatrix}}$$

therefore,

$$x = K^H_{HZ} = \frac{de - bf}{ad - bc} \qquad \text{Eq. 37}$$

$$y = K^H_{H_2Z} = \frac{af - ce}{ad - bc} \qquad \text{Eq. 38}$$

$$x/y = K^H_{H_2Z} = \frac{K^H_{H_2Z}}{K^H_{HZ}} \qquad \text{Eq. 39}$$

The activity, (MZ_n), of a species MZ_n formed in solution from a metal-ion, M, and a ligand, L, may be related to the activities of M, L, and the preceding complex ML_{n-1} by the Law of Mass Action. Thus,

$$(MZ_n) = {}^{T}\beta_n \ (M)(Z)^n = {}^{T}K_n \ (MZ_{n-1})(Z)$$

where the overall stability constant, ${}^{T}\beta_n$, is the activity quotient, or "thermodynamic" equilibrium constant for the reaction,

$$M + nZ \rightleftharpoons MZ_n$$

and the step stability constant, ${}^{T}K_n$, is the activity quotient for the particular reaction step,

$$MZ_{n-1} + Z \rightleftharpoons MZ_n.$$

Thus,

$${}^{T}\beta_o = {}^{T}K_o = 1 \quad \text{and} \quad {}^{T}\beta_1 = {}^{T}K_1.$$

Also, the overall and step constants are related by the expression,

$${}^{T}B_n = {}^{T}K_1, {}^{T}K_2 \ldots {}^{T}K_n = \overline{\prod^{n}} \ {}^{T}K_n.$$

The concentration of MZ_n is related to the concentrations of M, Z and MZ_{n-1} by the corresponding overall and step stiochiometric stability constants which are defined by,

$${}^{T}B_n = \frac{(MZ_n)}{(M)\ (Z)^n} = \frac{{}^{T}B_n}{\prod \sqrt{\nu_1}^{\nu_1}}$$

and

$$T_{K_n} = \frac{(MZ_n)}{(MZ_{n-1})(Z)} = \frac{T_{K_n}}{\Pi \gamma_i^{\nu_i}}$$

where ν_i are the stiochiometric coefficients of the participant species, and γ_i are their activity coefficients on the appropriate concentration scale.

The total bound chelating substance can be calculated starting with Eqs. 1, 2 and 8,

$$(M)_t = (M) + (MZ) + (MZ_2) \qquad \text{Eq. 1}$$

$$(Z)_t = \alpha(Z) + (MZ) + 2(MZ_2) \qquad \text{Eq. 2}$$

$$(H)_t = (2\cdot(Z)_t - (NaOH)) = (H) - (OH) + \beta(Z) \qquad \text{Eq. 8}$$

substituting Eq. 10 in Eq. 8, the expression becomes,

$$(Z) = \frac{2\cdot(Z)_t - (NaOH) - (H) + (OH)}{(H)\,K^H_{HZ} + 2(H)^2\,\overline{K}^H_{H_2Z}} = \qquad \text{Eq. 40}$$

$$(Z) = \frac{2\cdot(Z)_t - (NaOH) - (H) + (OH)}{\beta} \qquad \text{Eq. 41}$$

$$(MZ) = (Z)_t - \alpha(Z) \qquad \text{Eq. 2}$$

where (MZ) = total bound chelating substance.

Thus, the effective number of ligand molecules bound per metal-ion, which is $\bar{n}$, is,

$$\bar{n} = \frac{(MZ)}{(M)_t} \qquad \text{Eq. 42}$$

The values of $\bar{n}$ are plotted against pZ. The value of pZ corresponding to $\bar{n} = 0.5$ is assumed to be log K^{M}_{MZ}, and,

$$pZ = -\log (Z). \qquad \text{Eq. 43}$$

A table of metal complexes with organic and inorganic ligands has been published by the Chemical Society[14].

A concise summary of other methods in studying equilibria is given in the recent publication of Rossotti and Rossotti[15].

II

EXPERIMENTAL

A. BASICITY CONSTANTS

The hydrogen-ion concentration was measured in a solution containing known amounts of chelating substance, perchloric acid and sodium perchlorate. The experiments were performed as titrations with standardized NaOH by adding small increments of NaOH and measuring the pH after each addition. A constant temperature of 30.000°C ± 0.002°C was maintained.

PROCEDURE

Solutions of "Disec" and "Symaminol" (0:1) made up according to the specifications given on pages 92 and 93 were titrated at 30°C in an atmosphere of CO_2-free nitrogen. Measured increments of NaOH (0.1031 N) were added; the solution was stirred thoroughly to ensure complete reaction, homogenity and thermal equilibruim. The stirrer was cut off and the solution was allowed to become motionless before each pH reading was observed and recorded. No drift of the pH reading was observed when the solution was allowed to stand.

B. STABILITY CONSTANTS OF COMPLEXES

The hydrogen-ion concentration was measured in a solution containing known amounts of metal-ion, chelating substance, perchloric acid and sodium perchlorate. The experiments were performed as titrations with standardized NaOH by adding small increments of NaOH and measuring the pH after each addition. A constant temperature of $30.000^{\circ}C \pm 0.002^{\circ}C$ was maintained.

PROCEDURE

Solution of "Disec" and "Symaminol" with Copper II, perchloric acid and sodium perchlorate made up according to the specifications given on page 92 and 93 were titrated at $30^{\circ}C$ in an atmosphere of CO_2-free nitrogen. The metal-legand ratio for the solutions of "Disec" and "Symaminol" in each case were 0.2:1, 0.5:1, 1:1 and 10:1. Measured increments of NaOH (0.1031 N) were added; the solution was stirred thoroughly to ensure complete reaction, homogenity and thermal equilibrium. The stirrer was cut off and the solution was allowed to become motionless before each pH reading was observed and recorded. No drift of pH reading was observed when the solution was allowed to stand.

C. DATA AND TITRATION CURVES

TITRATION WITH NaOH

Cu - Disec (0 : 1)

Cu(II) 0

Disec.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II
0.0000	4.0850	4.0850
0.1000	4.7348	4.7359
0.2000	5.2441	5.2439
0.2500	5.4016	5.4011
0.3500	5.6500	5.6485
0.4000	5.7590	5.7598
0.5000	5.9430	5.9428
0.6000	6.1142	6.1145
0.7000	6.3022	6.3028
0.8000	6.4850	6.4850
0.9000	6.7045	6.7040
1.0000	6.9520	6.9509
1.1000	7.1910	7.1903
1.2500	7.5390	7.5402
1.5000	7.9812	7.9817
1.6000	8.1627	8.1624
1.7500	8.4324	8.4317
2.0000	9.1880	9.1895
2.1000	9.5890	9.5910
2.2000	9.8685	9.8695
2.3000	10.0575	10.0572
2.5000	10.2950	10.2942
2.7500	10.4624	10.4631
3.0000	10.5870	10.5876
3.5000	10.7600	10.7587

TITRATION WITH NaOH

Cu - Disec (0.2 : 1)

Cu(II) 0.2×10^{-3} M

Disec.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II
0.0000	3.6804	3.6802
0.1000	3.7925	3.7925
0.2000	3.9814	3.9815
0.3000	4.1560	4.1562
0.4000	4.8980	4.8978
0.5000	5.2281	5.2280
0.6000	5.5612	5.5615
0.7000	5.7450	5.7450
0.8000	5.9198	5.9195
0.9000	6.0940	6.0935
1.0000	6.3157	6.3154
1.1000	6.4540	6.4540
1.2000	6.6919	6.6915
1.3000	6.9287	6.9288
1.4000	7.1061	7.1065
1.5000	7.3249	7.3242
1.6000	7.5360	7.5355
1.7000	7.7280	7.7280
1.9000	8.0495	8.0499
2.0000	8.2353	8.2360
2.1500	8.5311	8.5305
2.2000	8.6590	8.6596
2.3000	8.8982	8.8980
2.4000	9.1766	9.1760
2.5000	9.4560	9.4561
2.6000	9.6480	9.6485
2.7000	9.8195	9.8198
2.8000	9.9455	9.9450
2.9000	10.0441	10.0435
3.0000	10.1292	10.1287
3.1000	10.1990	10.2000
3.2000	10.2615	10.2610
3.3000	10.3068	10.3060
3.4000	10.3510	10.3501
3.5000	10.3938	10.3950
3.7500	10.4747	10.4750
4.0000	10.5440	10.5437

TITRATION WITH NaOH

Cu - Disec (0.5 : 1)

Cu(II) 0.5×10^{-3} M

Disec.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II
0.0000	3.4368	3.4368
0.1000	3.5297	3.5295
0.3000	3.5910	3.5910
0.4000	3.7650	3.7647
0.5000	3.8700	3.8803
0.6200	4.0232	4.0231
0.7200	4.2383	4.2385
0.9100	4.5042	4.5040
1.0000	4.8541	4.8535
1.1000	5.1911	5.1916
1.2000	5.3661	5.3660
1.4000	5.7160	5.7163
1.5000	5.8990	5.8990
1.6000	6.1398	6.1398
1.7000	6.3316	6.3315
1.8000	6.5641	6.5643
1.9200	6.8200	6.8198
2.1000	7.4658	7.4655
2.2500	7.8164	7.8160
2.5000	8.2751	8.2750
2.6000	8.4860	8.4861
2.7000	8.6365	8.6364
2.8000	8.8020	8.8028
2.9000	9.0160	9.0157
3.0200	9.3474	9.3472
3.1000	9.5368	9.5365
3.2000	9.6980	9.6980
3.3000	9.8477	9.8480
3.4000	9.9515	9.9510
3.5000	10.0715	10.0715
3.6000	10.1273	10.1271
3.7500	10.2064	10.2069
4.2500	10.3681	10.3685
4.5000	10.4710	10.4715

TITRATION WITH NaOH

Cu - Disec (1 : 1)

Cu(II) 1×10^{-3} M

Disec.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II
0.0000	3.3324	3.3324
0.1200	3.4238	3.4245
0.2000	3.5262	3.5260
0.3000	3.5460	3.5460
0.4000	3.6496	3.6500
0.5000	3.6800	3.6795
0.6000	3.7060	3.7060
0.7000	3.7220	3.7225
0.8000	3.8170	3.8171
0.9000	3.8863	3.8869
1.0000	3.9220	3.9215
1.1000	4.0065	4.0065
1.2000	4.1014	4.1015
1.3000	4.1540	4.1540
1.4000	4.2630	4.2628
1.5000	4.3660	4.3663
1.6000	4.4895	4.4894
1.7000	4.6010	4.6011
1.8200	4.7850	4.7855
1.9000	4.8983	4.8987
2.0000	5.1185	5.1181
2.1000	5.2950	5.2950
2.2000	5.5560	5.5561
2.3000	5.6420	5.6424
2.6500	6.3325	6.3322
2.9200	7.2560	7.2560
3.0100	7.5576	7.5570
3.1000	7.8440	8.8441
3.2000	8.0461	8.0455
3.3000	8.1640	8.1644
3.4500	8.3950	8.3945
3.6000	8.6935	8.6930
3.7000	8.8885	8.8881
3.8500	9.1805	9.1800
4.0000	9.4250	9.4247
4.1000	9.6550	9.6551

Cu - Disec (1 : 1) (Continued)

milliliters of NaOH added	pH I	pH II
4.2000	9.7460	9.7460
4.4500	10.0562	10.0560
4.6000	10.1590	10.1597
4.7000	10.2640	10.2643
5.0000	10.3935	10.3937
5.5000	10.5562	10.5560

TITRATION WITH NaOH

Cu - Disec (10 : 1)

Cu(II) 10×10^{-3} M

Disec.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

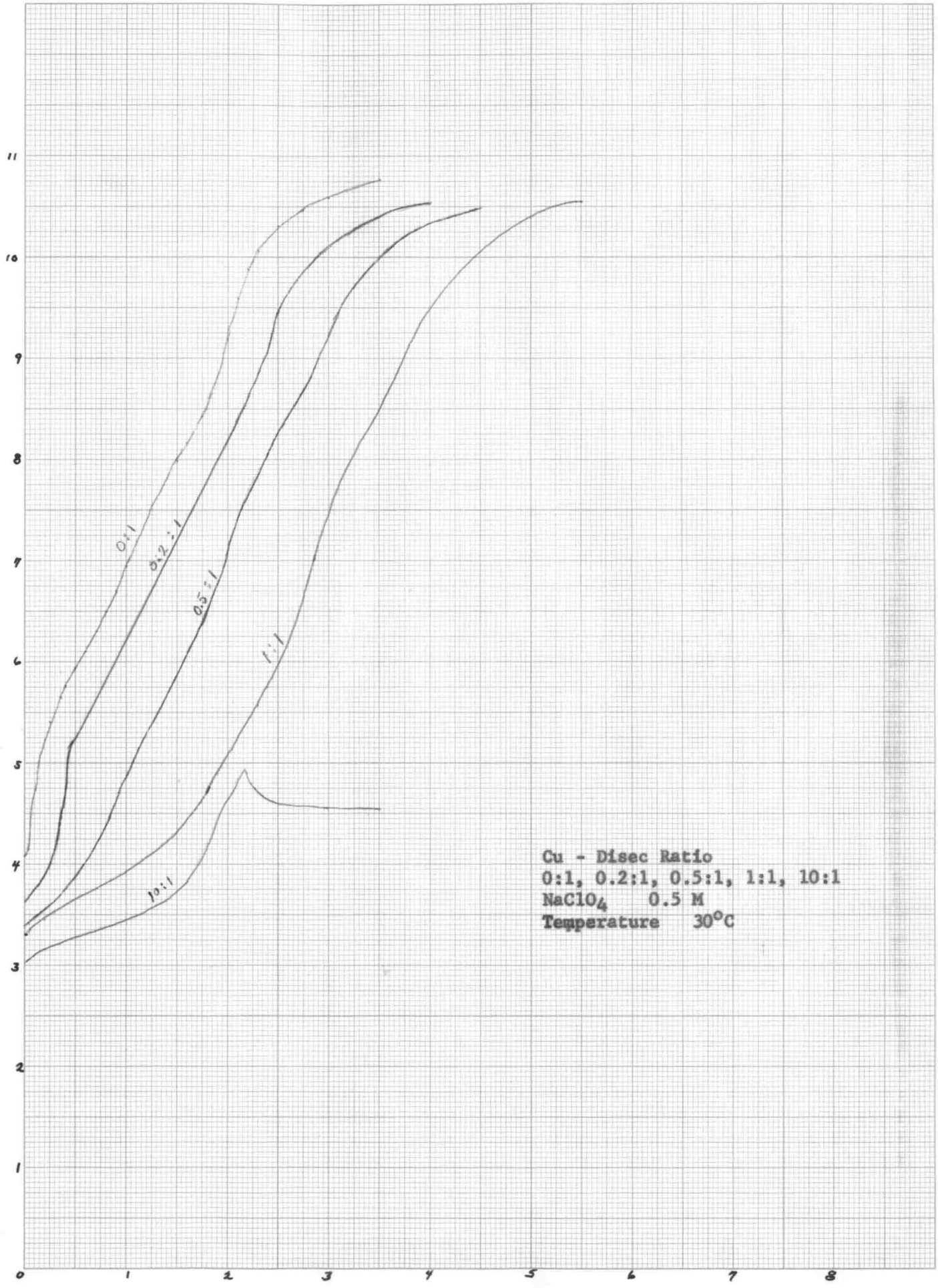
NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added		pH I	pH II
0.0000		3.0580	3.0580
0.1000		3.1243	3.1233
0.2100		3.1525	3.1529
0.3000		3.1935	3.1925
0.4500		3.2770	3.2772
0.5000		3.3060	3.3070
0.6000		3.3320	3.3310
0.8250		3.4075	3.4075
0.9500		3.4323	3.4329
1.0500		3.4810	3.4800
1.2000		3.5500	3.5488
1.3000		3.6050	3.6042
1.4000		3.6525	3.6529
1.5000		3.7412	3.7420
1.6000		3.8314	3.8320
1.7500		4.1200	4.1215
1.8500		4.3470	4.3482
1.9500		4.6217	4.6202
2.0500		4.7460	4.7469
2.1500	ppt.	4.9450	ppt. 4.9460
2.3000		4.6770	4.6770
2.4000		4.6450	4.6459
2.6000		4.6270	4.6275
2.7500		4.5895	4.5893
3,0000		4.5893	4.5890
3.5000		4.5892	4.5888

VOLUME OF NaOH (ml.)

Copper(II) - Disec
TITRATION WITH NaOH



Cu - Disec Ratio
0:1, 0.2:1, 0.5:1, 1:1, 10:1
$NaClO_4$ 0.5 M
Temperature 30°C

TITRATION WITH NaOH

Cu - Symaminol (0 : 1)

Cu(II) 0

Symaminol . $2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II	pH III
0.0000	5.1860	5.1860	5.1860
0.1500	6.1150	6.1145	6.1157
0.2000	6.3120	6.3109	6.3120
0.3000	6.6462	6.6450	6.6455
0.4000	6.9410	6.9400	6.9400
0.5000	7.2240	7.2231	7.2256
0.6000	7.5157	7.5150	7.5168
0.7000	7.8464	7.8464	7.8475
0.8000	8.1264	8.1250	8.1275
0.9000	8.3610	8.3600	8.3598
1.0000	8.5555	8.5570	8.5559
1.1000	8.7012	8.7004	8.7000
1.2000	8.8375	8.8400	8.8369
1.3000	8.9445	9.9458	8.9432
1.4000	9.0472	9.0459	9.0465
1.5000	9.1465	9.1455	9.1465
1.6000	9.2334	9.2321	9.2346
1.7500	9.3580	9.3600	9.3575
1.8000	9.3975	9.3990	9.3982
1.9000	9.4720	9.4711	9.4705
2.0000	9.5455	9.5440	9.5455
2.1000	9.6155	9.6160	9.6173
2.2000	9.6831	9.6825	9.6840
2.3000	9.7468	9.2475	9.7461
2.4000	9.8104	9.8090	9.8117
2.5000	9.8676	9.8698	9.8665
2.6000	9.9250	9.9230	9.9257
2.7500	10.0075	10.0052	10.0086
2.9000	10.0814	10.0800	10.0821
3.0000	10.1276	10.1259	10.1280
3.2500	10.2390	10.2398	10.2407
3.5000	10.3340	10.3325	10.3356
3.7500	10.4200	10.4187	10.4208
4.0000	10.5000	10.5017	10.5020
4.5000	10.6350	10.6372	10.6329
5.5000	10.8405	10.8395	10.8420

TITRATION WITH NaOH

Cu - Symaminol (0.2 : 1)

Cu(II) 0.2×10^{-3} M

Symaminol.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II	pH III
0.0000	4.2575	4.2575	4.2575
0.1000	4.5323	4.5302	4.5309
0.2000	4.7443	4.7491	4.7438
0.3000	5.2454	5.2425	5.2419
0.4100	5.7000	5.6950	5.6981
0.5000	6.1181	6.1175	6.1208
0.6000	6.4137	6.4149	6.4119
0.7500	6.8451	6.8464	6.8410
0.8500	7.2592	7.2641	7.2625
0.9500	7.5780	7.5811	7.5753
1.0500	7.8600	7.8640	7.8631
1.2000	8.2857	8.2831	8.2891
1.3000	8.4600	8.4585	8.4562
1.4000	8.5931	8.5905	8.5945
1.5000	8.7261	8.7305	8.7317
1.6500	8.9374	8.9351	8.9332
1.7500	9.0420	9.0363	9.0425
1.8500	9.1604	9.1633	9.1649
2.0500	9.3141	9.3175	9.3192
2.2000	9.4168	9.4210	9.4219
2.3000	9.4902	9.4871	9.4852
2.4500	9.5446	9.5491	9.5435
2.5500	9.6063	9.6108	9.6051
2.7500	9.7820	9.7865	9.7818
3.0000	9.9020	9.9061	9.9005
3.5000	10.1206	10.1175	10.1218
4.0000	10.3100	10.3125	10.3142
5.0000	10.5511	10.5559	10.5501

TITRATION WITH NaOH

Cu - Symaminol (0.5 : 1)

Cu(II) 0.5×10^{-3} M

Symaminol.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II	pH III
0.0000	4.1423	4.1423	4.1423
0.1000	4.2743	4.2765	4.2740
0.2500	4.5520	4.5503	4.5542
0.3500	4.7020	4.7010	4.7000
0.4500	5.0174	5.0200	5.0165
0.6000	5.0776	5.0809	5.0761
0.7500	5.3020	5.3020	5.3045
0.9000	5.552	5.5790	5.5725
1.0000	5.7580	5.7500	5.7505
1.1500	6.1300	6.1265	6.1272
1.2500	6.5400	6.5374	6.5390
1.3500	6.9937	6.9981	6.9962
1.5000	7.8104	7.8138	7.7075
1.6000	8.1885	8.1905	8.1922
1.7000	8.4170	8.4204	8.4147
1.8000	8.5472	8.5512	8.5457
1.9000	8.6810	8.6774	8.6792
2.0000	8.8534	8.8500	8.8545
2.1000	8.9800	8.9768	8.9811
2.2500	9.1617	9.1583	9.1572
2.5000	9.4160	9.4192	9.4144
3.0000	9.7474	9.7515	9.7509
3.2500	9.8930	9.8880	9.8895
3.5000	9.9810	9.9834	9.9848
3.7500	10.0780	10.0754	10.0770
4.0000	10.2420	10.2386	10.2475
4.5000	10.3900	10.3952	10.3961
5.0000	10.4751	10.4729	10.4763

TITRATION WITH NaOH

Cu - Symaminol (1 : 1)

Cu(II) 1×10^{-3} M

Symaminol.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added	pH I	pH II	pH III
0.0000	3.9810	3.9810	3.9810
0.1000	4.2015	4.2005	4.2029
0.2000	4.3195	4.3207	4.3187
0.3000	4.4400	4.4387	4.4415
0.5000	4.6295	4.6285	4.6302
0.6000	4.7613	4.7602	4.7590
0.8000	4.9765	4.9780	4.9753
0.9000	5.1040	5.1022	5.1035
1.0000	5.2560	5.2550	5.2569
1.1500	5.5087	5.5072	5.5098
1.2520	5.8795	5.8806	5.8783
1.5000	6.4526	6.4539	6.4540
1.6000	6.5983	6.5969	6.6005
1.7500	6.7680	6.7602	6.7657
1.9000	6.9466	6.9490	6.9475
2.0000	7.0630	7.0610	7.0605
2.1000	7.2038	7.2055	7.2045
2.2500	ppt. 7.7117	ppt. 7.7100	ppt. 7.7136
2.3500	7.9867	7.9885	7.9850
2.5000	8.1555	8.1572	8.1539
2.6100	8.5340	8.5327	8.5320
2.8000	8.8150	8.8127	8.8170
2.9000	8.9476	8.9495	8.9460
3.0000	9.0820	9.0800	9.0829
3.2500	9.3580	9.3605	9.3571
3.5000	9.5787	9.5775	9.5805
3.6000	9.6480	9.6460	9.6495
3.7500	9.7614	9.7595	9.7624
4.0000	9.9083	9.9115	9.9090
4.5000	10.1437	10.1400	10.1459
5.0000	10.3185	10.3172	10.3208
6.0000	----	----	----

TITRATION WITH NaOH

Cu - Symaminol (10 : 1)

Cu(II) 10×10^{-3} M

Symaminol.$2HClO_4$ 1×10^{-3} M

$NaClO_4$ 0.5 M

Temperature 30.000°C

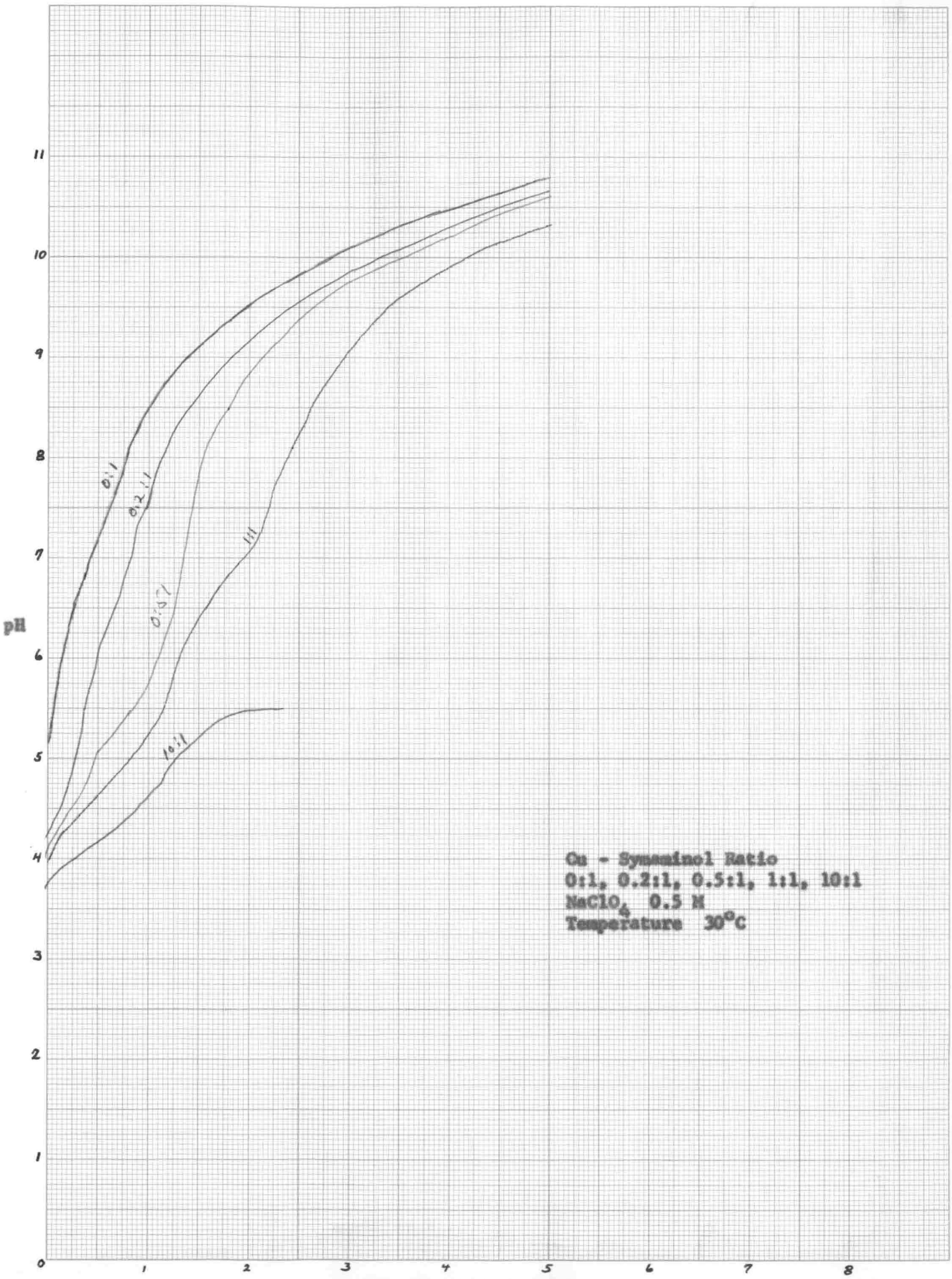
NaOH 0.1031 M

Volume of Solution 100 ml.

milliliters of NaOH added		pH I	pH II		pH III
0.0000		3.7440	3.7440		3.7440
0.1000		3.9032	3.9000		3.8984
0.2000		3.9644	3.9698		3.9640
0.3000		4.0722	4.0739		4.0708
0.4500		4.1436	4.1415		4.1461
0.5500		4.2081	4.2075		4.2123
0.6000		4.2665	4.2704		4.2652
0.7500		4.4038	4.4011		4.3991
0.8500		4.4600	4.6310		4.4641
1.0000		4.5740	4.5702		4.5754
1.1000		4.8242	4.8291		4.8273
1.2000		4.9260	4.9297		4.9243
1.3000		4.9800	4.9769		4.9811
1.4000		5.1291	5.1316		5.1328
1.5500		5.3210	5.3192		5.3226
1.6500		5.3407	5.3415		5.3376
1.7500		5.4283	5.4317		5.4325
1.8500		5.4567	5.4598		5.4970
2.0100	ppt.	5.5012	5.4976	ppt.	5.4900
2.1000		5.5007	5.4975		5.4911
2.2500		5.4985	5.4961		5.4903
2.5000		5.4980	5.4926		5.4905
3.0000		5.4963	5.4912		5.4891

Values below are unsteady.

Copper(II) - Symaminol
TITRATION WITH NaOH



D. SAMPLE CALCULATIONS

BASICITY CONSTANTS

$V_1 = 0.5000$ ml.

$H_1 = 1.1402484 \times 10^{-6}$ (pH = 5.9430)

$N = 0.1031$ M

$Z = 1 \times 10^{-3}$ M

$K_w = 1.471 \times 10^{-14}$

(values chosen from data on page 21).

$$g_1 = 2 - \frac{V_1 N}{Z \cdot 100} + \frac{K_w - (H_1)^2}{H_1 \cdot Z \left(\frac{100}{100+V_1}\right)} \qquad \text{Eq. 29}$$

$$g_1 = \frac{0.5 \text{ ml.} \times 0.1031 \text{ M}}{.001 \text{ M} \times 100} + \frac{1.471 \times 10^{-14} - (1.1402484 \times 10^{-6} \text{ M})^2}{1.1402484 \times 10^{-6} \text{ M} \times .001 \times \frac{100}{100+0.50 \text{ ml.}}}$$

$g_1 = 1.4833670$

$V_2 = 1.6000$ ml.

$H_2 = 6.8754248 \times 10^{-9}$ M (pH = 8.1627)

$N = 0.1031$ M

$Z = 1 \times 10^{-3}$ M

$K_w = 1.471 \times 10^{-14}$

(values chosen from data on page 21).

$$g_2 = 2 - \frac{V_2 N}{Z \cdot 100} + \frac{K_w - (H_2)^2}{H_1 \cdot Z \left(\frac{100}{100+V_2}\right)} \qquad \text{Eq. 30}$$

$$g_2 = 2 - \frac{1.6 \text{ ml.} \times 0.1031 \text{ M}}{.001 \text{ M} \times 100} + \frac{1.471 \times 10^{-14} - (6.8754248 \times 10^{-9} \text{ M})^2}{6.8754248 \times 10^{-9} \text{ M} \times .001 \text{ M} \times \frac{100}{100+1.6 \text{ ml.}}}$$

$g_2 = 0.35255345$

Substituting appropriate values for g_1, H_1 and g_2, H_2 in the following equations,

$$\underbrace{(g_1 - 1)(H)\, K^{H}_{HZ}}_{a} + \underbrace{(g_1 - 2)(H)^2\, K^{H}_{H_2Z}}_{b} = \underbrace{-g_1}_{c} \qquad \text{Eq. 31}$$

$$\underbrace{(g_2 - 1)(H)\, K^{H}_{HZ}}_{c} + \underbrace{(g_2 - 2)(H)^2\, K^{H}_{H_2Z}}_{d} = \underbrace{-g_2}_{f} \qquad \text{Eq. 32}$$

The results are two simultaneous equations which are solved by using determinants (see page 13).

Therefore,

$K^{H}_{HZ} = 7.8040423 \times 10^{7}$ $\qquad \log K^{H}_{HZ} = 7.905256$

$K^{H}_{H_2Z} = 6.6242990 \times 10^{13}$ $\qquad \log K^{H}_{H_2Z} = 13.795393$

$K^{H}_{H_2Z} = 8.4882920 \times 10^{5}$ $\qquad \log K^{H}_{H_2Z} = 5.688687$

STABILITY CONSTANTS

$$K^{H}_{HZ} = 7.8040423 \times 10^{7}$$

$$\bar{K}^{H}_{H_2Z} = 6.6242990 \times 10^{13}$$

$$H = 1.168623 \times 10^{-7} \text{ M} \quad (pH = 6.3157)$$

$$(Z)_t = 1 \times 10^{-3} \text{ M}$$

$$(M)_t = 0.2 \times 10^{-3} \text{ M}$$

(values chosen from data on pages 22 and 36).

$$\beta = (H)(K^{H}_{HZ}) + 2(H)^2 \bar{K}^{H}_{H_2Z} \qquad \text{Eq. 10}$$

$$\beta = 7.31063$$

$$\alpha = 1 + (H) K^{H}_{HZ} + (H)^2 \bar{K}^{H}_{H_2Z} \qquad \text{Eq. 7}$$

$$\alpha = 11.02464707$$

$$(Z) = \frac{2(Z)_t - (NaOH) - (H) + (OH)}{\beta} \qquad \text{Eq. 40}$$

$$(Z) = 1.39622 \times 10^{-5}$$

$$(MZ) = (Z)_t - \alpha(Z) \qquad \text{Eq. 2}$$

$$\bar{n} = \frac{(MZ)}{(M)_t} = 1.17818 \qquad \text{Eq. 42}$$

$$pZ = -\log (Z) \qquad \text{Eq. 43}$$

$$pZ = -\log (1.39622 \times 10^{-5})$$

$$pZ = 4.85511$$

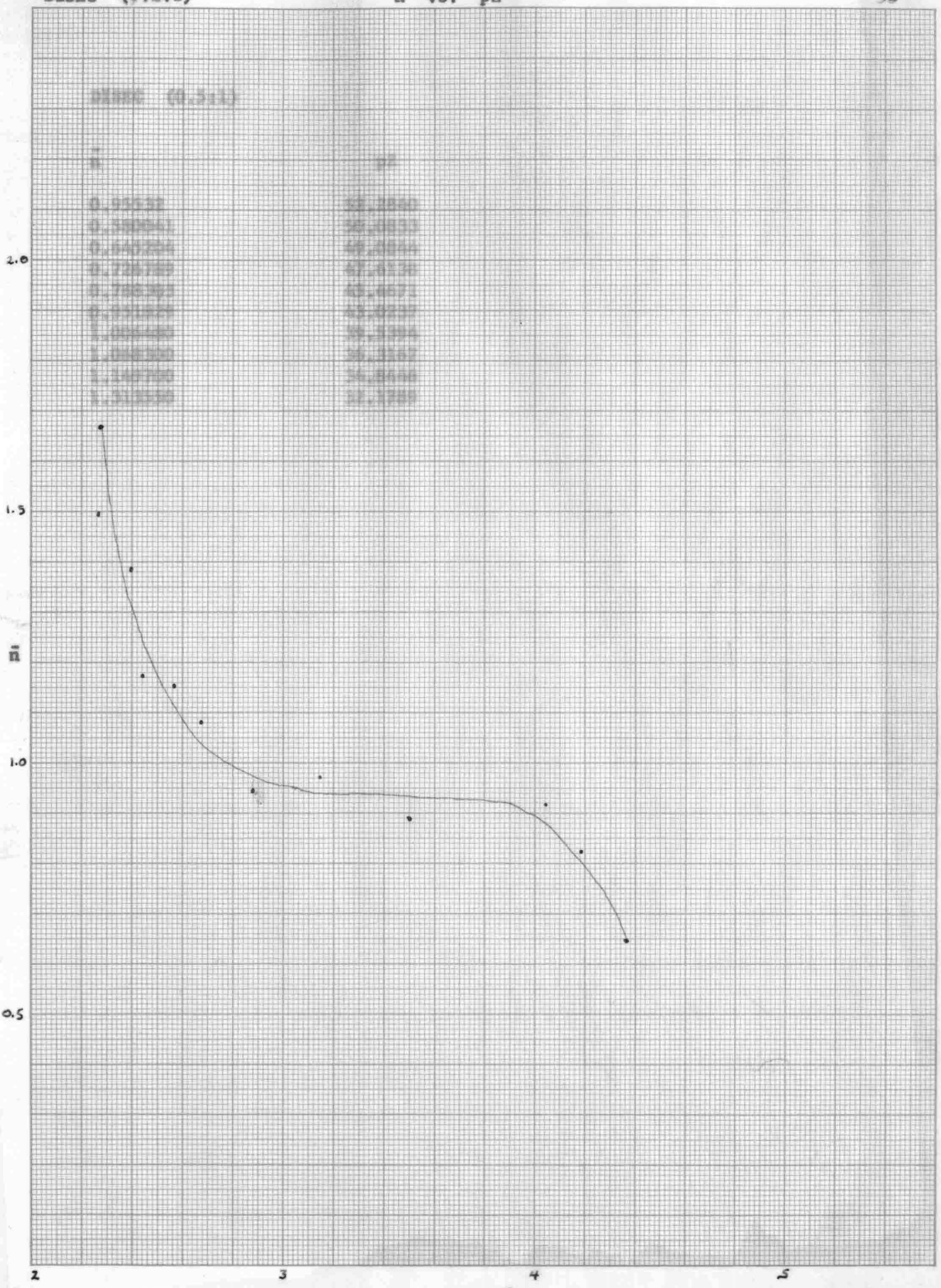
III

EVALUATION OF DATA

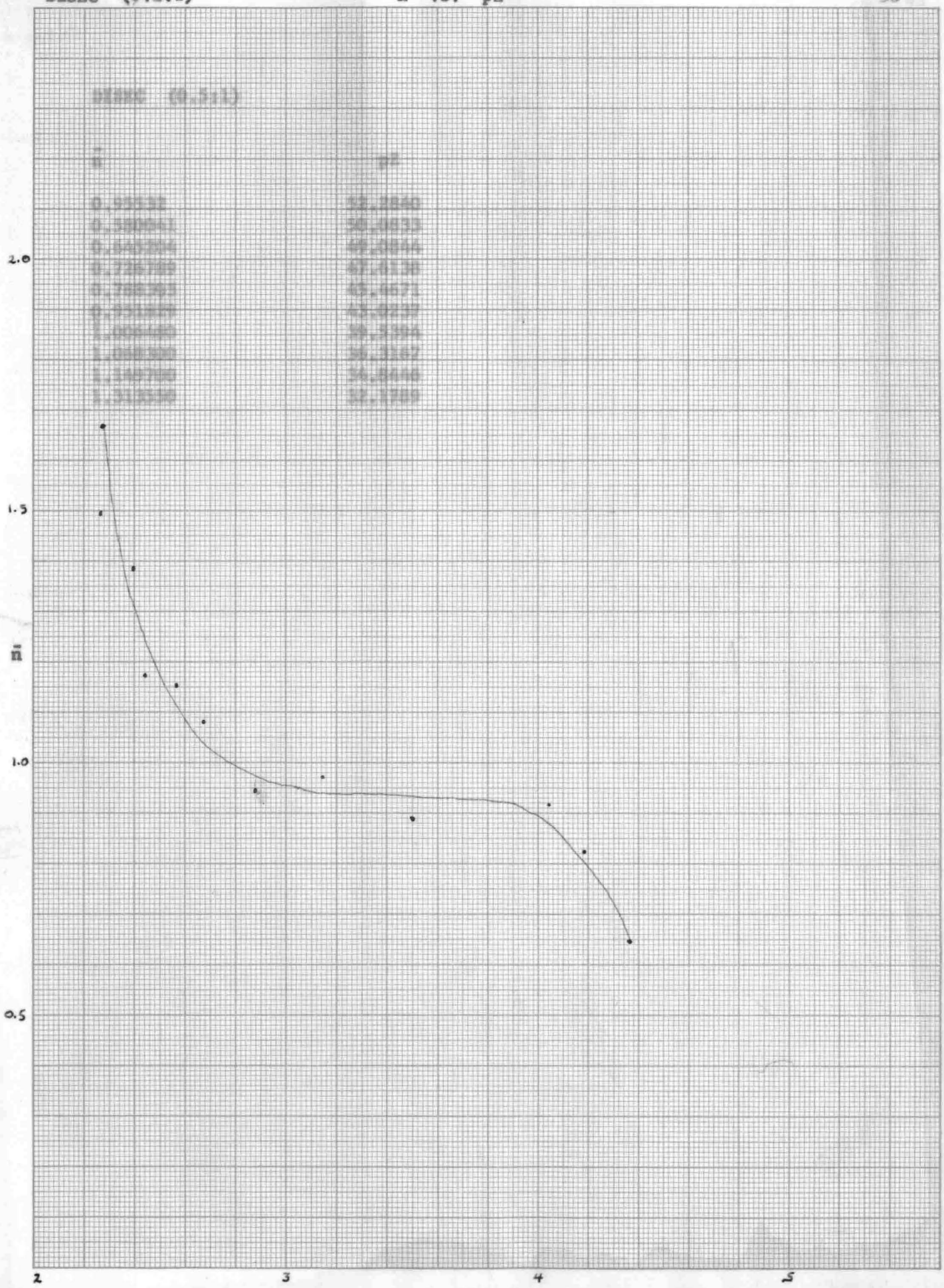
From plots of $\bar{n}$ vs. pZ, it can be seen that the Copper-Disec complex and the Copper-Symaminol complex are in the ratio of 1:1.

DISEC (0.2:1)

$\bar{n}$	pZ
0.645484	49.3152
0.753256	47.3809
0.914423	45.6333
0.887171	37.9176
0.967347	34.6781
0.939082	31.3376
1.010330	29.9727
1.079610	28.5795
1.154350	27.2913
1.178180	25.7455
1.382080	24.9712
1.497140	23.6084
1.627520	22.4261

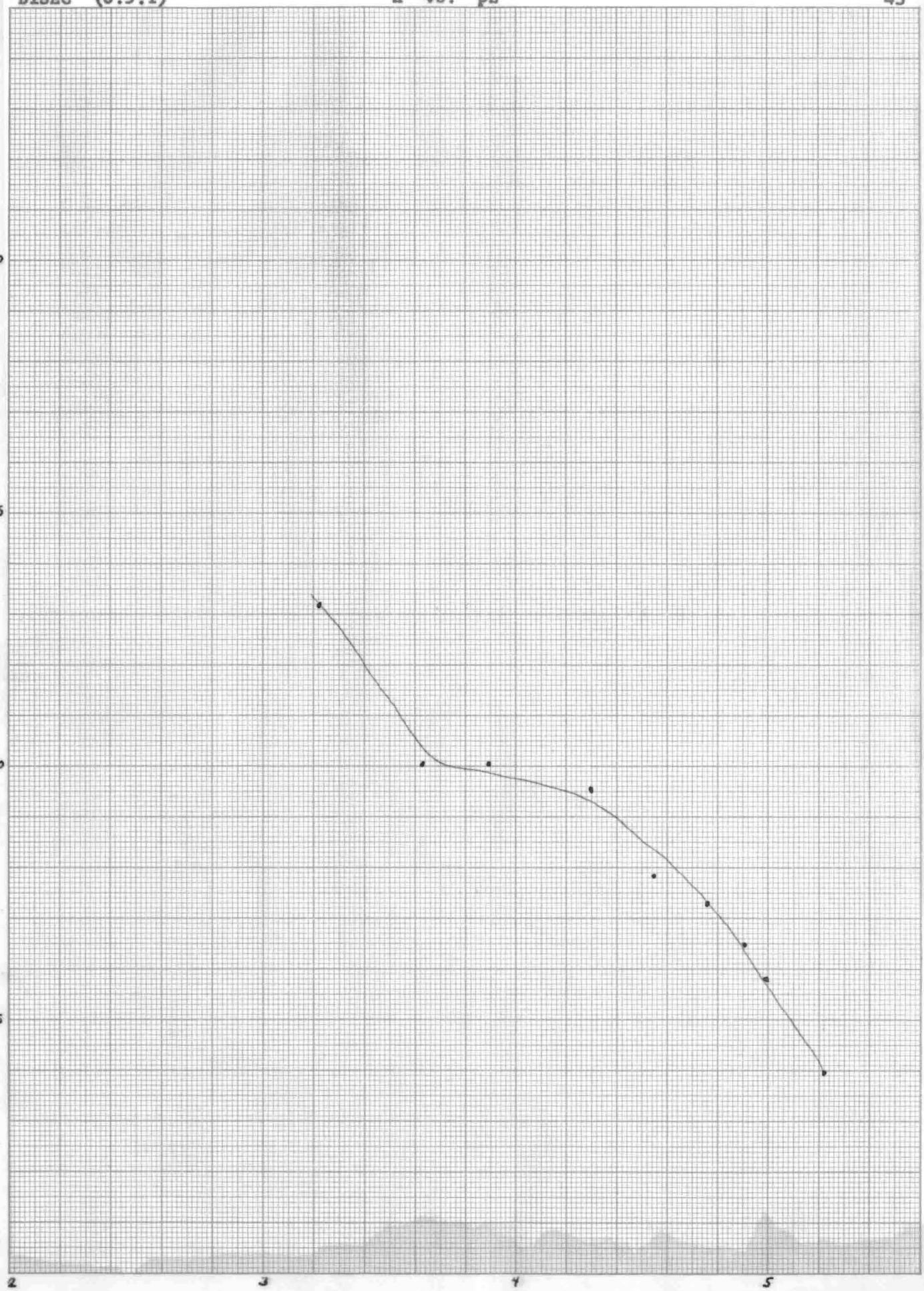

2.0
1.5
1.0
0.5
$\bar{n}$
2
3
4
5
pZ x 10^{-1}

DISEC (0.2:1) $\bar{n}$ vs. pZ



DISEC (0.5:1)

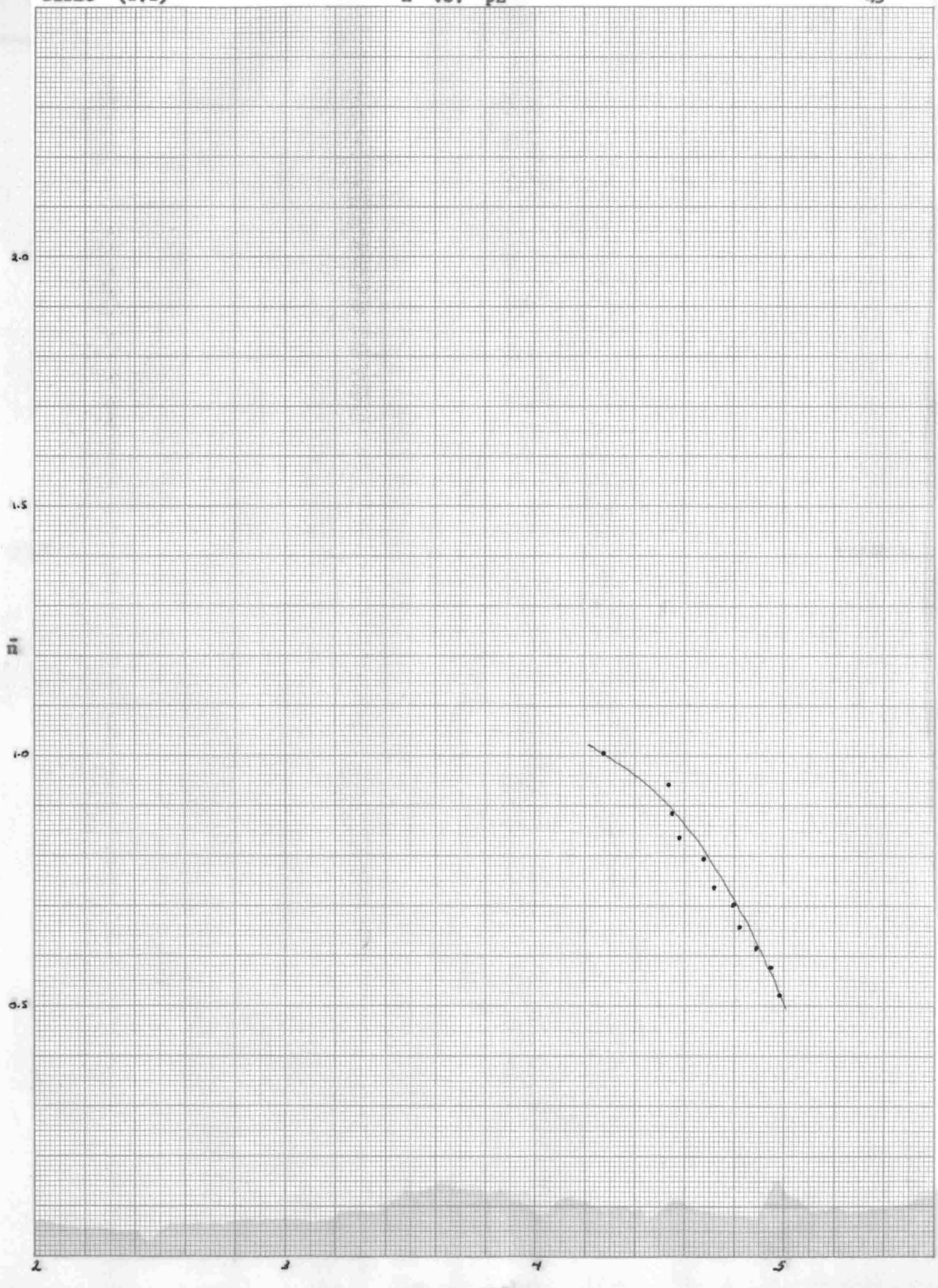
$\bar{n}$	pZ
0.95532	52.2840
0.580041	50.0833
0.645204	49.0844
0.726789	47.6138
0.788393	45.4671
0.951829	43.0237
1.006480	39.5394
1.068300	36.3167
1.149700	34.8446
1.313550	32.1789


2.0
1.5
$\bar{n}$
1.0
0.5
2
3
4
5
pZ x 10^{-1}

DISEC (1:1)

$\bar{n}$	pZ
0.527374	49.7504
0.573857	49.6143
0.614571	48.9563
0.656142	48.2217
0.703226	48.0096
0.746692	47.2314
0.792331	46.6118
0.838420	45.9023
0.886543	45.5599
0.944706	45.3205
1.037390	42.8604

$\bar{n}$ vs. pZ

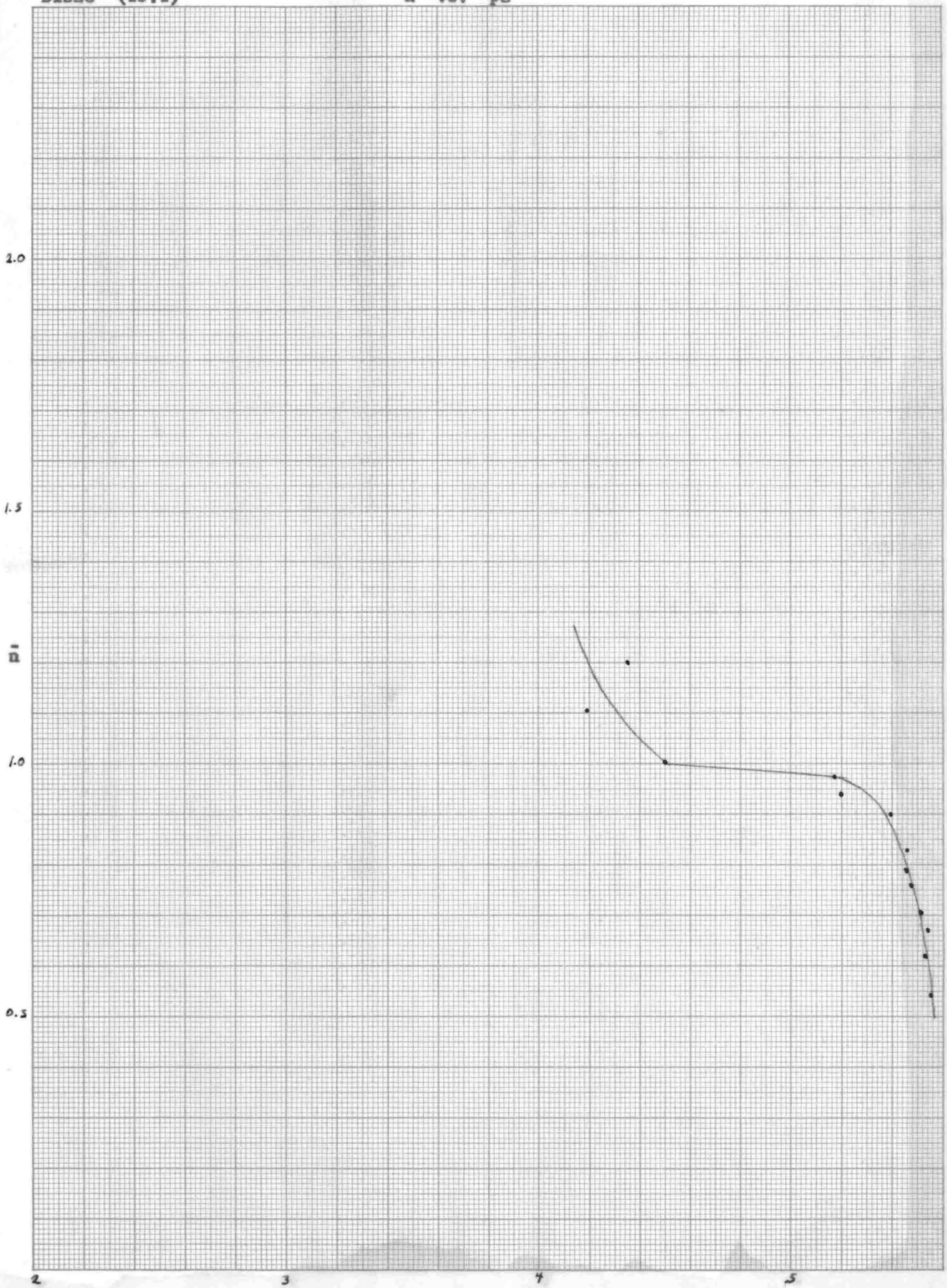


DISEC (10:1)

$\bar{n}$ (x 10)	pZ
0.505553	55.7765
0.542912	55.6843
0.621979	55.3273
0.675751	55.4209
0.707674	55.1462
0.760712	54.8803
0.795437	54.6617
0.834114	54.6441
0.864909	54.1813
0.899297	53.9069
0.940260	52.0692
0.976276	51.8150
1.068030	45.2486
1.119760	41.9189
1.201760	43.4613

DISEC (10:1)

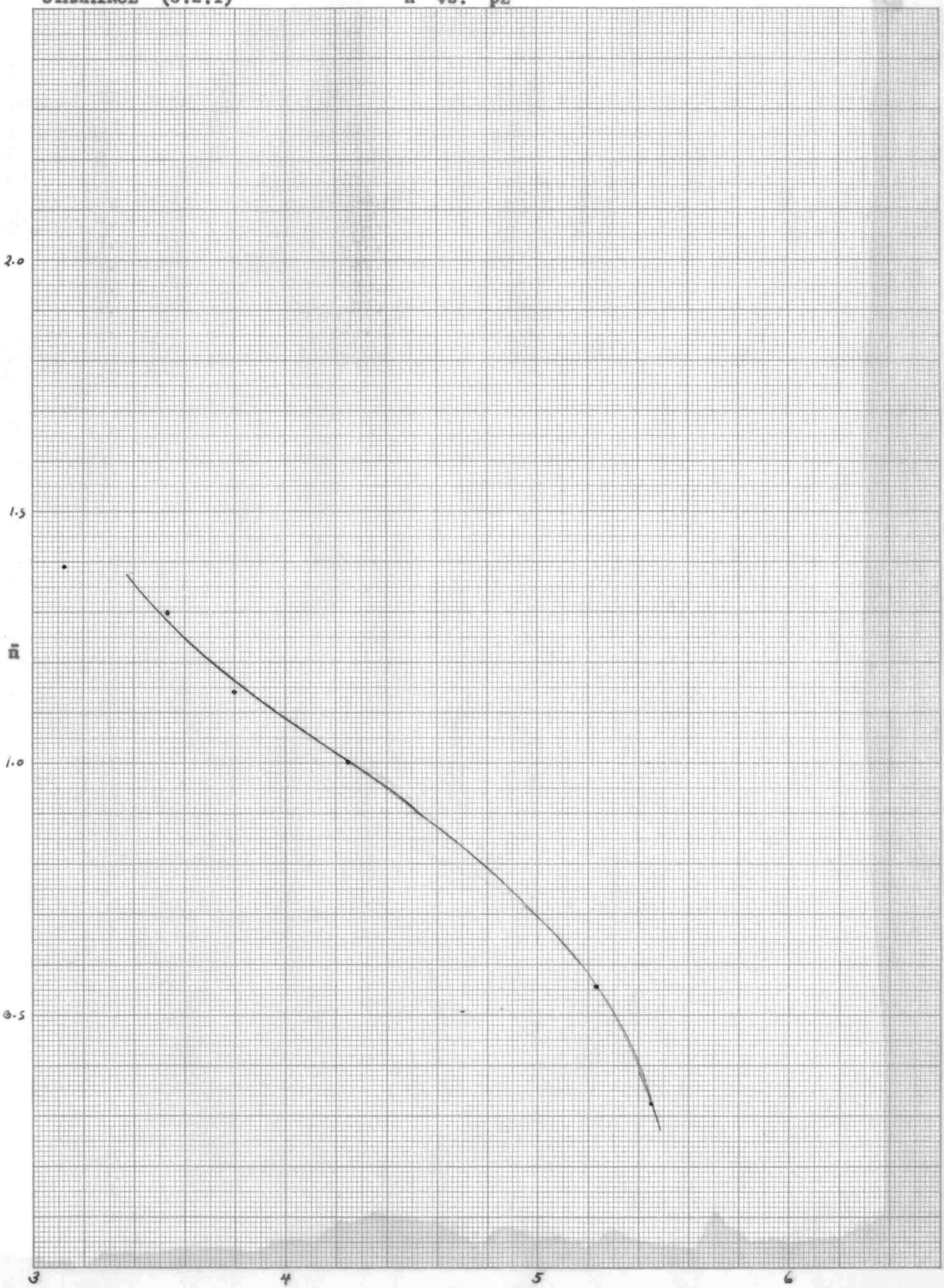
$\bar{n}$ vs. pZ



SYMAMINOL (0.2:1)

$\bar{n}$	pZ
0.326373	54.4539
0.553139	52.3253
0.505892	47.0032
1.002490	42.5011
1.147710	38.2622
1.293620	35.3794
1.388080	3.13505

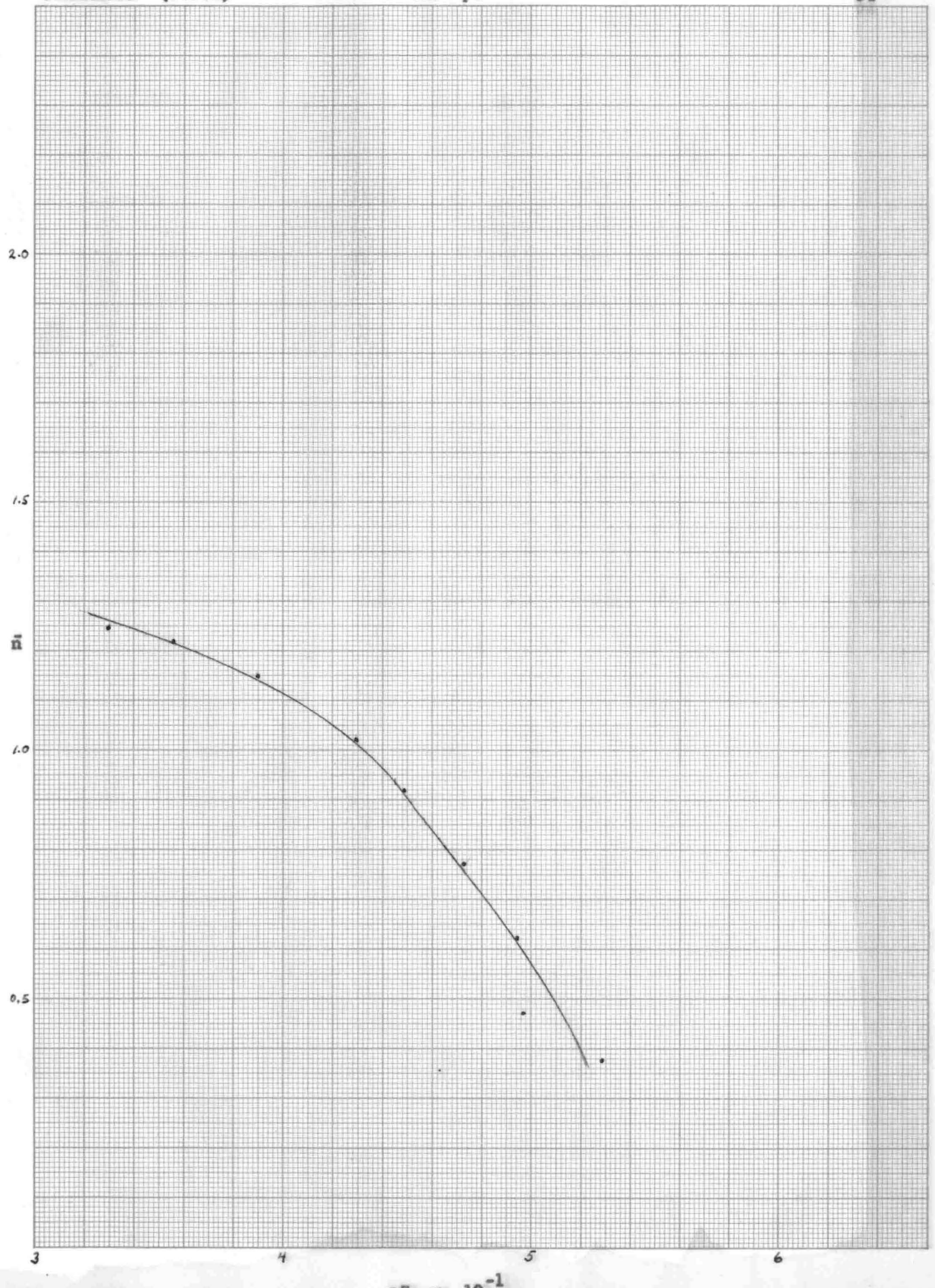
SYMAMINOL (0.2:1) $\bar{n}$ vs. pZ



SYMAMINOL (0.5:1)

$\tilde{n}$	pZ
0.378299	52.9895
0.468773	49.7865
0.622029	49.3965
0.770856	47.2944
0.919128	44.9304
1.016150	43.0277
1.154190	39.5370
1.220680	35.6399
1.249110	31.5634

SYMAMINOL (0.5:1) $\bar{n}$ vs. pZ

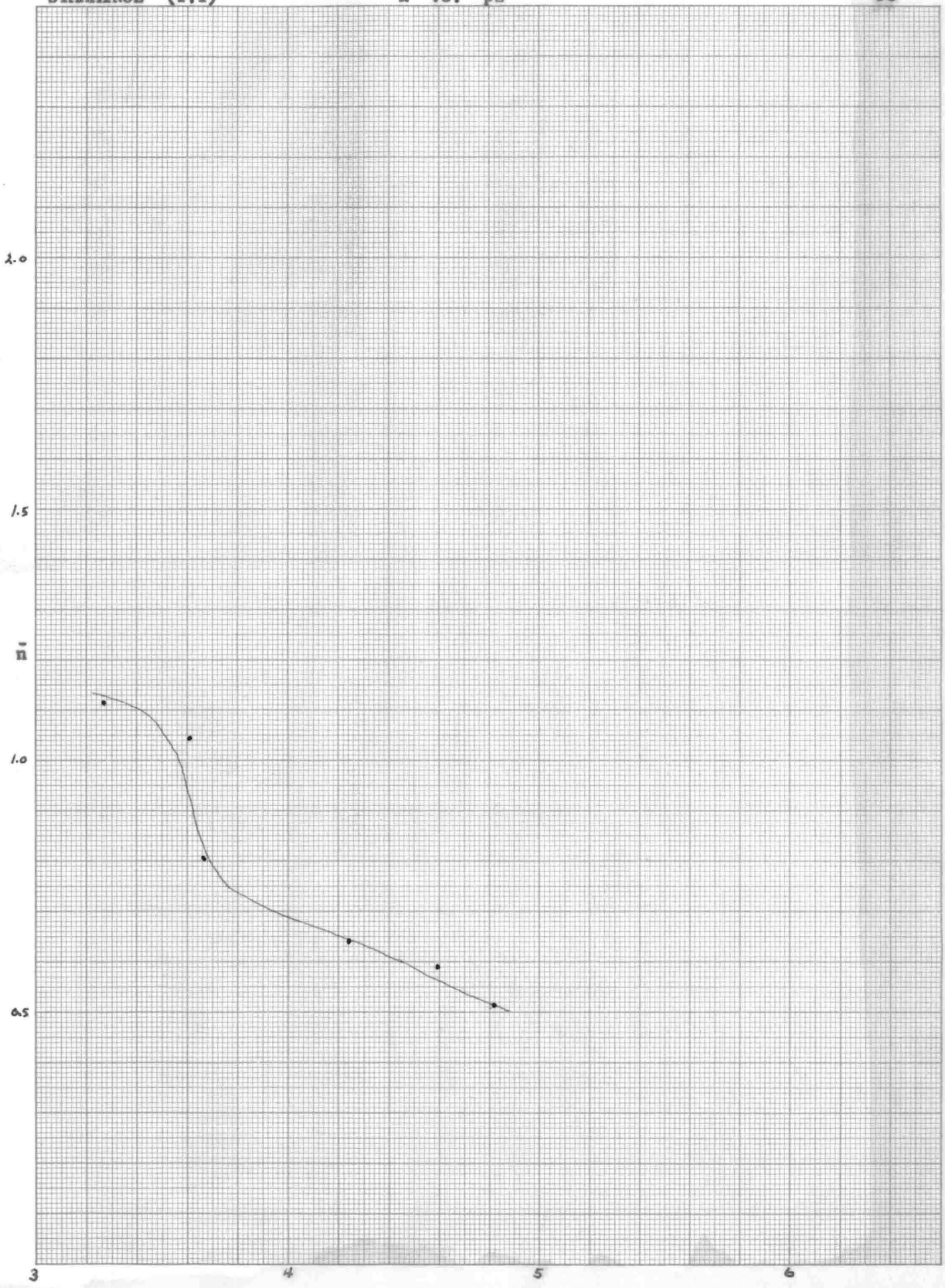


SYMAMINOL (1:1)

$\bar{n}$	pZ
0.590440	46.0629
0.638074	42.4765
0.755301	37.5693
0.805905	36.6918
0.887205	36.3517
1.037170	36.1951
1.110170	32.6667

SYMAMINOL (1:1)

$\bar{n}$ vs. pZ

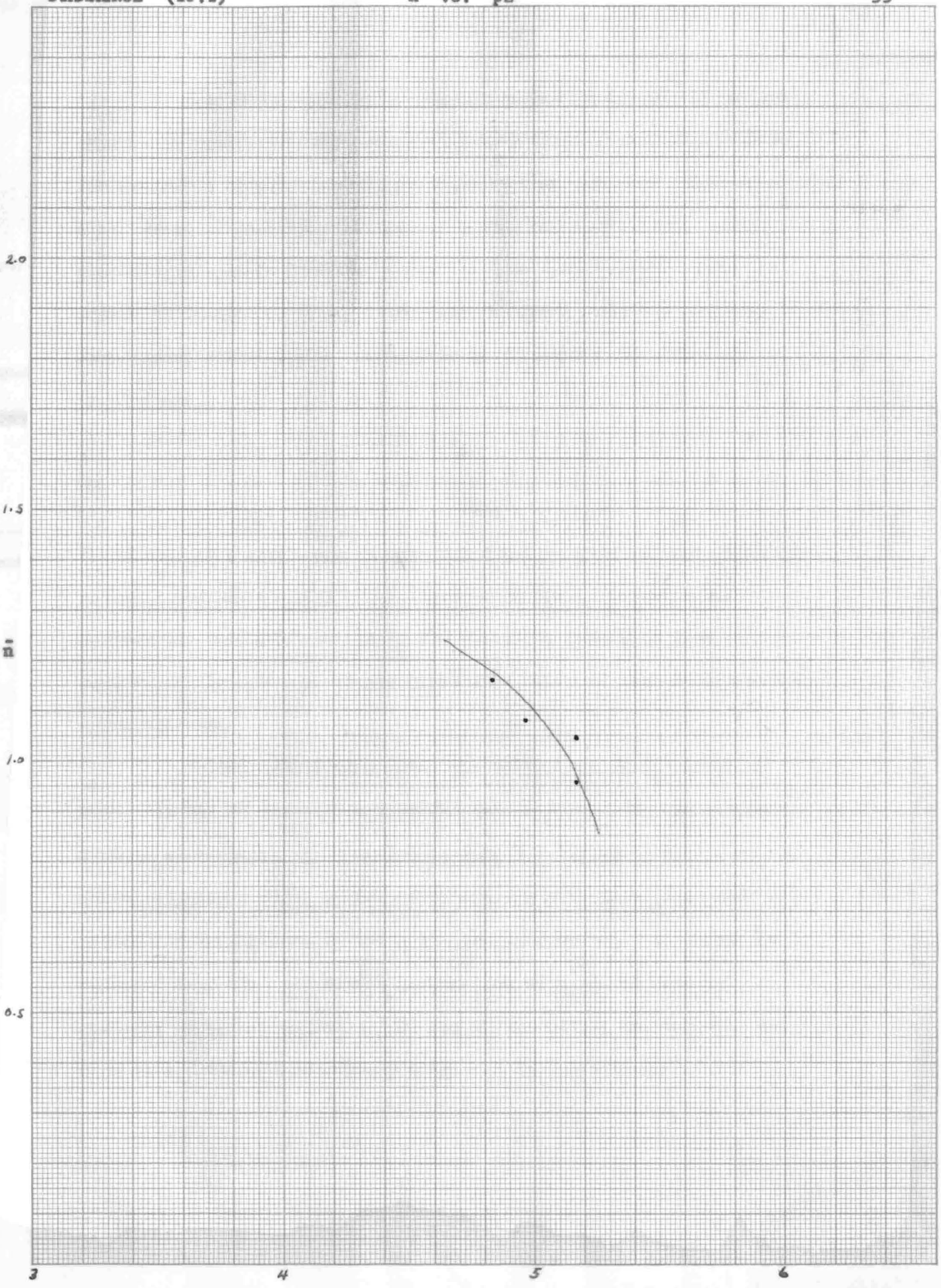


SYMAMINOL (10:1)

$\tilde{n}$ (x 10)	pZ
0.955066	51.7147
1.038120	51.6291
1.084960	49.7908
1.163030	48.3163

SYMAMINOL (10:1)

$\bar{n}$ vs. pZ



Some understanding of the values and limits of the methods used to determine Basicity and Stability Constants were investigated. The graphical method as given by Schwarzenbach and Baur suggested that values of Stability Constants be obtained as follows: each pair of experimental values, $\bar{n}$ and Z (where $\bar{n}$ equals the average number of ligands, Z, bound to one central group; and Z equals the concentration of free Z), is used to calculate a pair of values (x,y) where,

$$x \equiv 1/K_{MZ}$$

$$y \equiv K_{MZ_2}.$$

The values of x and y are in turn set equal to zero and the equation solved. The values of x and y are then plotted. Schwarzenbach derives the "correct" values of the Stability Constants from that portion of the curve where the greatest density of line intersections seems apparent.

In this particular work, the values were not plotted as such, but all of the values were fed into the computer and compared against each other. This method is somewhat superior to that of the actual graphical plots of Schwarzenbach, as many more lines and points can be analyzed by using the computer method. It should be recorded here that one entire computation of a set of data by ordinary methods requires a full day to calculate; the computer has made this problem a relatively simple on in comparison.

A summary of the Stability Constant Data obtained from "Disec" and "Symaminol" by the computer is given in the following chart,

"DISEC"

	$\bar{n}_1$	Z_1	$\bar{n}_2$	Z_2	K^M_{MZ}	$K^M_{MZ_2}$
1.	8.87×10^{-1}	7.07×10^{-8}	1.08	4.08×10^{-6}	1.10×10^{8}	2.19×10^{4}
2.	9.39×10^{-1}	1.13×10^{-6}	1.38	1.95×10^{-5}	8.35×10^{6}	3.23×10^{4}
3.	1.01	2.23×10^{-6}	1.18	1.39×10^{-5}	1.82×10^{7}	1.60×10^{4}
4.	1.08	4.07×10^{-6}	1.50	3.53×10^{-5}	1.02×10^{7}	2.83×10^{4}
5.	9.14×10^{-1}	2.48×10^{-9}	1.98	7.93×10^{-5}	4.23×10^{9}	5.57×10^{5}
6.	1.01	2.23×10^{-6}	1.38	1.95×10^{-5}	7.42×10^{6}	3.24×10^{4}
7.	6.45×10^{-1}	5.01×10^{-10}	1.15	7.14×10^{-6}	3.63×10^{9}	2.56×10^{4}
8.	7.53×10^{-1}	1.16×10^{-9}	1.01	2.23×10^{-6}	2.63×10^{9}	4.76×10^{3}

"SYMAMINOL"

1.	1.30	2.11×10^{-7}	.924	1.03×10^{-4}	2.08×10^{7}	-6.66×10^{2}
2.	1.15	6.16×10^{-8}	1.46	1.65×10^{-4}	1.27×10^{8}	5.22×10^{3}
3.	1.15	5.97×10^{-6}	.931	3.74×10^{-5}	1.17×10^{6}	-2.26×10^{3}
4.	1.00	9.58×10^{-10}	1.29	2.11×10^{-7}	1.19×10^{12}	1.98×10^{6}
5.	7.65×10^{-1}	1.27×10^{-9}	1.80	1.89×10^{-4}	2.57×10^{9}	2.11×10^{4}
6.	9.31×10^{-1}	3.74×10^{-5}	1.16	1.37×10^{-4}	1.80×10^{5}	1.74×10^{3}
7.	3.27×10^{-1}	5.35×10^{-11}	.927	1.03×10^{-4}	9.07×10^{9}	-6.62×10^{2}
8.	5.53×10^{-1}	1.35×10^{-10}	1.00	9.58×10^{-9}	9.14×10^{9}	1.49×10^{6}

From the data it can be concluded that in making calculations where it is necessary to solve simultaneous equations by use of a set of data from titration curves, one must be careful not to choose values in the set of data that are too close; in like manner not too far from each other. In choosing values in the mid-range of the titration curves, K_1 and K_2 will both be significant with respect to each other. One will find values of Basicity and Stability Constants in close agreement if the data values are in a region where both equilibrium constants are of the same order.

Also, if one wishes to find out by equilibrium studies which species are present in a certain system, there are three necessary requirements,

1. Constant ionic medium (to keep the activity coefficients constant)
2. As high accuracy as possible
3. As broad a range of concentrations as possible.

The subject of solution chemistry suggests the importance of a knowledge of the mechanism of the reactions of the coordinated compounds. Much has been accomplished in this field[16]; the keen interest in it suggests a future of significant contributions.

IV

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V

AUTOBIOGRAPHY

I, Ronald Weston Davis, was born in Hopewell, Virginia, 29 November, 1936. My elementary and high school education was received in the Hopewell City School System. I attended Hampden-Sydney College from September, 1955 to June, 1959, receiving the degrees of Bachelor of Science and Bachelor of Arts.

I began my graduate work in Chemistry at Purdue University, after which I transferred to the University of Richmond Graduate School, September, 1962. I was granted the Puryear Fellowship during the term 1963-1964. I am a candidate for the Degree of Master of Science in Chemistry at the University of Richmond in August, 1964.

VI

APPENDIX

A. TABLE OF REAGENTS

The following reagents were used throughout the course of the experiment:

1. Cupric Nitrate, $Cu(NO_3)_2 \cdot 3H_2O$ (Reagent Grade)
   J. T. Baker Chemical Company
   Lot No. 23070
2. Sodium Hydroxide, NaOH (Reagent Grade)
   Mallinckrodt Chemical Works
   Lot No. 6704
3. Potassium Acid Phthalate, $KHC_8H_4O_4$ (Reagent Grade)
   J. T. Baker Chemical Company
   Lot No. 22242
4. Perchloric Acid, $HClO_4$ 60-62% (Reagent Grade)
   J. T. Baker Chemical Company
   Lot No. 23406
   and
   General Chemical Division, Allied Chemical and Dye Corporation
   Lot No. S-211
5. Potassium Chloride, KCl saturated solution (Reagent Grade)
   Beckman 3502 saturated KCl solution
   Beckman Instruments, Inc.
   Cat. No. 289-003903
6. Ethyl Ether (Absolute) $C_2H_5OC_2H_5$ (Analytical Reagent)
   Mallinckrodt Chemical Works
   Cat. No. 0848

7. Ethyl Alcohol (absolute) C_2H_5OH (Reagent Grade)

   U. S. Industrial Chemical Company

   New York, New York

8. Methyl Alcohol (absolute) CH_3OH (Reagent Grade)

   J. T. Baker Chemical Company

   Phillipsburg, New Jersey

   Cat. No. 9070

9. Amberlite IRA - 400 (Cl type) Synthetic Ion Exchange Resin

   Analytical Grade

   Rohm and Haas

   Philadelphia, Pennsylvania

   Lot No. 7308

10. Epichlorohydrin $CH_2 - CH - CH_2 - Cl$ (Reagent Grade)

    O

    (1,-chloro-2-3-epoxypropane)

    Matheson, Coleman and Bell

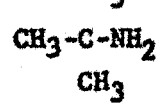
    Division of Matheson Company, Inc.

    Norwood, Ohio

    Lot No. Ex 55

11. 2-amino-2-(hydroxymethyl)-1,3-propanediol (Reagent Grade)

$$HOCH_2-\overset{\displaystyle CH_2OH}{\overset{|}{C}}-CH_2OH$$
$$\quad\quad\quad

12. tertiary - Butylamine  (Reagent Grade)

L. Light and Company, Ltd.

Colonbrook, England

B. SPECIAL APPARATUS AND EQUIPMENT

The following apparatus and equipment was used throughout the course of the experiment:

1. Sargent-Slomin Electrolytic Analyzer

   E. H. Sargent and Company, Chicago, Illinois

   Cat. No. S-29465

2. Platinum Electrodes, Heavy Duty

   Phipps and Bird, Richmond, Virginia

   Cat. No. 32-872, 32-873

3. Fisher Melting Point Apparatus

   Fisher Scientific Company, Pittsburg, Pennsylvania

   Cat. No. 13-947-S

4. E. H. Sargent and Company Constant Temperature Bath ($\pm$0.01°C)

   with Pyrex Brand Glass Container

   Central Circulation and Heater Unit with Motor

   Thermoregulator

   Relay Unit

   Cat. No. S-84810

5. Fisher Inhibited Bath-oil (Stablized)

   Fisher Scientific Company, Fair Lawn, New Jersey

   Lot No. 731440

   Cat. No. O-5

6. Titration Cell, Simplified, Karl Fisher Type

   Arthur H. Thomas Company

   Cat. No. 4935-R

Titration Vessel (Glass Jar), 250 ml. capacity

with wide mouth and screw neck

Arthur H. Thomas Company

Cat. No. 4935-S

7. Magnetic Variable Stirrer

Mag-Mix, Precision Scientific, Chicago, Illinois

Cat. No. 65904

(Modified by enclosing in sealed aluminum case for use in bath-oil.)

8. Magnetic Stirrer, Teflon, dia. = 3/8", length = 1"

Phipps and Bird, Richmond, Virginia

Cat. No. 77-865-05

9. Cylinder Containing CO_2-free nitrogen (water-pumped)

Southern Oxygen Company, Richmond, Virginia

10. Beckman Research pH Meter

Beckman Instruments, Inc.

Scientific and Process Instruments Division

11. Beckman Glass Electrode, Silver-Silver Chloride Internals

Cat. No. 40498

Beckman Frit Junction Reference Electrode, Calomel Internals

Cat. No. 39071

Beckman Instruments, Inc.

12. Beckman Buffer Solutions

pH 4 (3506)

pH 7 (3581)

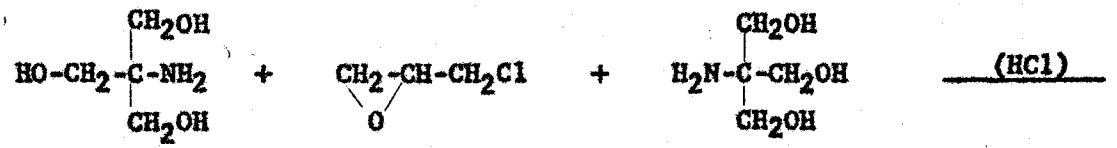
pH 10 (3505)

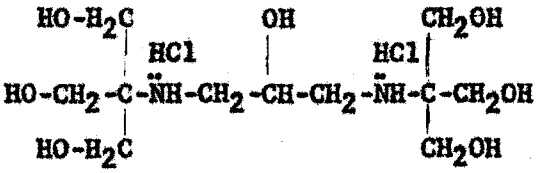
Beckman Instruments, Inc.

13. International Business Machines 1620 and 407

C. PREPARATION OF LIGANDS

Disec·2HCl



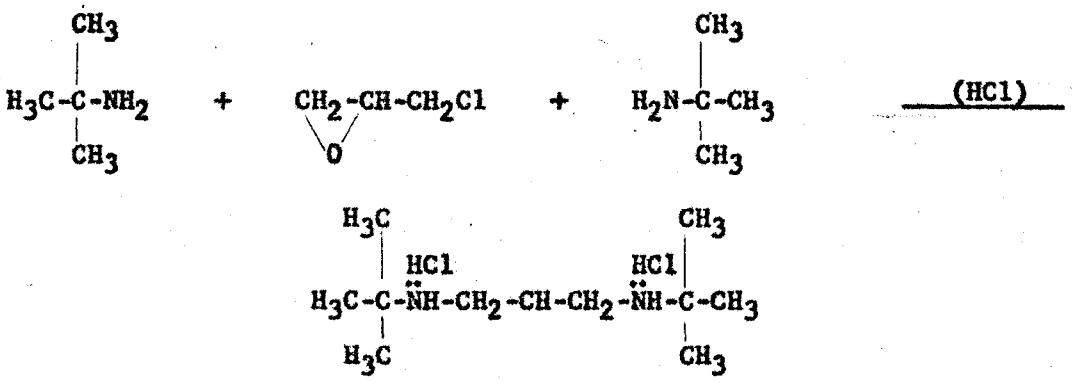


2,2,8,8-Tetrakishydroxymethyl-3,7-diaza-1,5,9-nonanetriol dihydrochloride

The compound was synthesized by adding one mole of epichlorohydrin to two moles of 2-amino-2-(hydroxymethyl)-1,3-propanediol in absolute ethyl alcohol in the manner given by Pierce and Wotiz.[17] The temperature was kept approximately 30°C. After the last addition of epichlorohydrin, solution was refluxed for six hours.

The dihydrochloride salt of "Disec" was prepared by bubbling dry HCl gas through the mixture for 15 minutes. The salt was recrystalized three times from absolute ethyl alcohol. The melting point of Disec·2HCl was 186-188°C (M.W.=371.28 g).

Symaminol·2HCl



2,2,8,8-Tetramethyl-3,7-diaza-5-nonaneol dihydrochloride

The compound was synthesized by adding one mole of epichlorohydrin to two moles of tertiary-butylamine in absolute ethyl alcohol in the manner given by Pierce and Wotiz.[17] The temperature was kept approximately 30°C. After the last addition of epichlorohydrin, the solution was refluxed for six hours.

The dihydrocholoride salt of "Symaminol" was prepared by bubbling dry HCl gas through the mixture for 15 minutes. The salt was recrystalized three times from absolute ethyl alcohol. The melting point of Symaminol·2HCl was 141-143°C (M.W.=275.28 g).

D. PREPARATION AND STANDARDIZATION OF SOLUTIONS

CUPRIC NITRATE-TRIHYDRATE, $Cu(NO_3)_2 \cdot 3H_2O$ STOCK SOLUTION

(M.W. = 241.604g)

A solution of cupric nitrate was prepared by dissolving 72.48 grams of the reagent in three liters of CO_2-free distilled water. The solution was filtered through glass wool to remove any undissolved substances. The Cu^{2+} solution was analyzed by the procedure in Standard Methods of Chemical Analysis[18] using platinum electrodes and an electrodeposition apparatus and depositing the copper from solution on the surface of the platinum electrodes.

DATA

50 milliliter aliquots used

	I	II	III
Weight of Platinum Electrode and deposited Copper	11.10770g	11.10770g	11.10770g
Weight of Platinum Electrode	10.77845	10.77845	10.77845
Weight of Copper Deposited	0.32925g	0.32925g	0.32925g

Average weight of Copper deposited = 0.32925g

$$\text{Concentration of Copper}^{2+}\text{ solution} = \frac{\text{grams Cu deposited}}{\text{At. wgt. Cu} \times \text{vol. Cu}^{2+}\text{ used}}$$

$$= \frac{0.32925\text{g}}{63.54\text{g/mole} \times 0.050\ \text{l.}}$$

$$= 0.1036\ \text{M}$$

SODIUM HYDROXIDE, NaOH STOCK SOLUTION

(M.W. = 39.9972g)

A solution of CO_2-free sodium hydroxide was prepared by standard methods by dissolving approximately 12 grams of NaOH in 12 grams of CO_2-free distilled water. The resulting 50/50 solution was filtered through a Gooch crucible containing asbestos matting as a filtering device to remove any insoluble carbonate ion. The filtrate was diluted to three liters and standardized by titrating the NaOH against a known weight of potassium acid phthalate (M.W. = 204.2286g) using 2% phenolphthalein solution as an indicator.

DATA

	I	II	III
Weight of $KHC_8H_4O_4$ and container	23.2522g	23.2522g	23.2522g
Weight of container	22.7217	22.7217	22.7217
Weight of $KHC_8H_4O_4$	0.5305g	0.5305g	0.5305g
Volume of NaOH to titrate $KHC_8H_4O_4$	= 25.20 ml.	25.20 ml.	25.20 ml.
Average weight of $KHC_8H_4O_4$	= 0.5305g		
Average volume of NaOH	= 25.20 ml.		

$$\text{Concentration of NaOH} = \frac{\text{weight of } KHC_8H_4O_4}{\text{M.W. of } KHC_8H_4O_4 \times \text{vol. of NaOH}}$$

$$= \frac{0.5305\text{g}}{204.2286\text{g/equiv.} \times 0.02520\text{ l.}}$$

$$= 0.1031\text{ N}$$

PERCHLORIC ACID, $HClO_4$ (60-62%) STOCK SOLUTION

(M.W. = 100.4685g)

A solution of perchloric acid (approximately o.1N) was prepared by addition of 50 grams of 60-62% $HClO_4$, and diluting the solution to three liters.

The $HClO_4$ solution was standardized by titrating a 25 ml. aliquot of standardized NaOH (0.1031N) with the $HClO_4$ using bromothymol blue as an indicator.

DATA

	I	II	III
Volume of NaOH	25 ml.	25 ml.	25 ml.
Normality of NaOH	0.1031 N	0.1031 N	0.1031 N
Volume of $HClO_4$	18.70 ml.	18.70 ml.	18.70 ml.

Average volume of $HClO_4$ = 18.70 ml.

$$\text{Concentration of } HClO_4 = \frac{\text{Vol. of NaOH} \times \text{normality of NaOH}}{\text{Vol. of } HClO_4}$$

$$= \frac{25 \text{ ml.} \times 0.1031 \text{ N}}{18.70 \text{ ml.}}$$

$$= 0.1378 \text{ M}$$

SODIUM PERCHLORATE, $NaClO_4$ STOCK SOLUTION

(M.W. = 122.4404g)

A solution of $NaClO_4$ was prepared by first preparing a solution of $HClO_4$ and then titrating the $HClO_4$ solution with NaOH to pH = 7.000.

STANDARDIZATION OF $HClO_4$ BY STOCK NaOH (0.1031 N)

In each case, the $HClO_4$ solution was diluted 10 ml. of $HClO_4$ to 100 ml. and 5 ml. of this solution was titrated with 0.1031 N NaOH

DATA

	I	II	III
Volume of $HClO_4$	5 ml.	5 ml.	5 ml.
Volume of NaOH	23.11 ml.	23.11 ml.	23.11 ml.
Normality of NaOH	0.1031 N	0.1031 N	0.1031 N

Average volume of NaOH used = 23.11 ml.

$$\text{Concentration of } HClO_4 = \frac{\text{Vol. of NaOH} \times \text{normality of NaOH}}{\text{Vol. of } HClO_4} \times \frac{100}{10}$$

$$= \frac{23.11 \text{ ml.} \times 0.1031 \text{ N}}{5 \text{ ml.}} \times \frac{100}{10}$$

$$= 4.7653 \text{ N}$$

(The 4.7653 N $HClO_4$ solution was titrated with an NaOH solution to pH = 7.000.) The total volume was measured and concentration of resulting $NaClO_4$ solution determined.

DATA

Volume of $HClO_4$	350 ml.
Normality of $HClO_4$	4.7653 N
Volume of NaOH	327.390 ml.

Total volume of solution = 677.390 ml.

CALCULATIONS TO DETERMINE CONCENTRATION OF $NaClO_4$ SOLUTION

Vol. of $HClO_4$ x Normality of $HClO_4$ = no. equiv. ClO_4^-

.350 l. x 4.7653 N = 1.6678 equiv.

$$\text{Concentration of } NaClO_4 = \frac{\text{no. equiv.} \times 1000}{\text{Total vol. of solution}}$$

$$= \frac{1.6678 \text{ equiv.} \times 1000}{.677390 \text{ l.}}$$

$$= 2.4622 \text{ N}$$

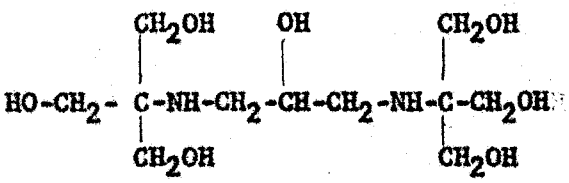
(The 2.4622 N $NaClO_4$ solution is diluted with H_2O to give a concentration of 2.0 N.)

$$\text{Volume of solution needed} = \frac{\text{Normality of } NaClO_4 \times \text{Vol. of } NaClO_4}{\text{Desired Normality}}$$

$$= \frac{2.4622 \text{ N} \times 677.390 \text{ ml.}}{2.0000 \text{ N}}$$

= 833.924 ml. (final concentration = 2.0 N)

"DISEC" STOCK SOLUTION



(M.W. = 298.339g)

Approximately 3.7 grams of Disec·2HCl* (M.W. = 371.28g) was dissolved in 500 ml. of CO_2-free distilled water. The solution was then passed through an Amberlite column (IRA-400, Cl type converted to OH form). The resulting solution was tested by addition of $AgNO_3$ solution. No chloride ion was found to be present.

The "Disec" free-base solution was titrated with standardized $HClO_4$ to determine its concentration.

DATA

50 ml. aliquots used

$$\text{Concentration of "Disec"} = \frac{\text{Vol. of } HClO_4 \times \text{Normality of } HClO_4}{\text{Vol. of "Disec"}}$$

$$= \frac{4.650 \text{ ml.} \times 0.1378 \text{ N}}{50 \text{ ml.}}$$

$$= 0.01282 \text{ N} \qquad (0.00541 \text{ M})$$

*Preparation of Disec·2HCl is given on page 71.

STANDARDIZATION OF DISEC

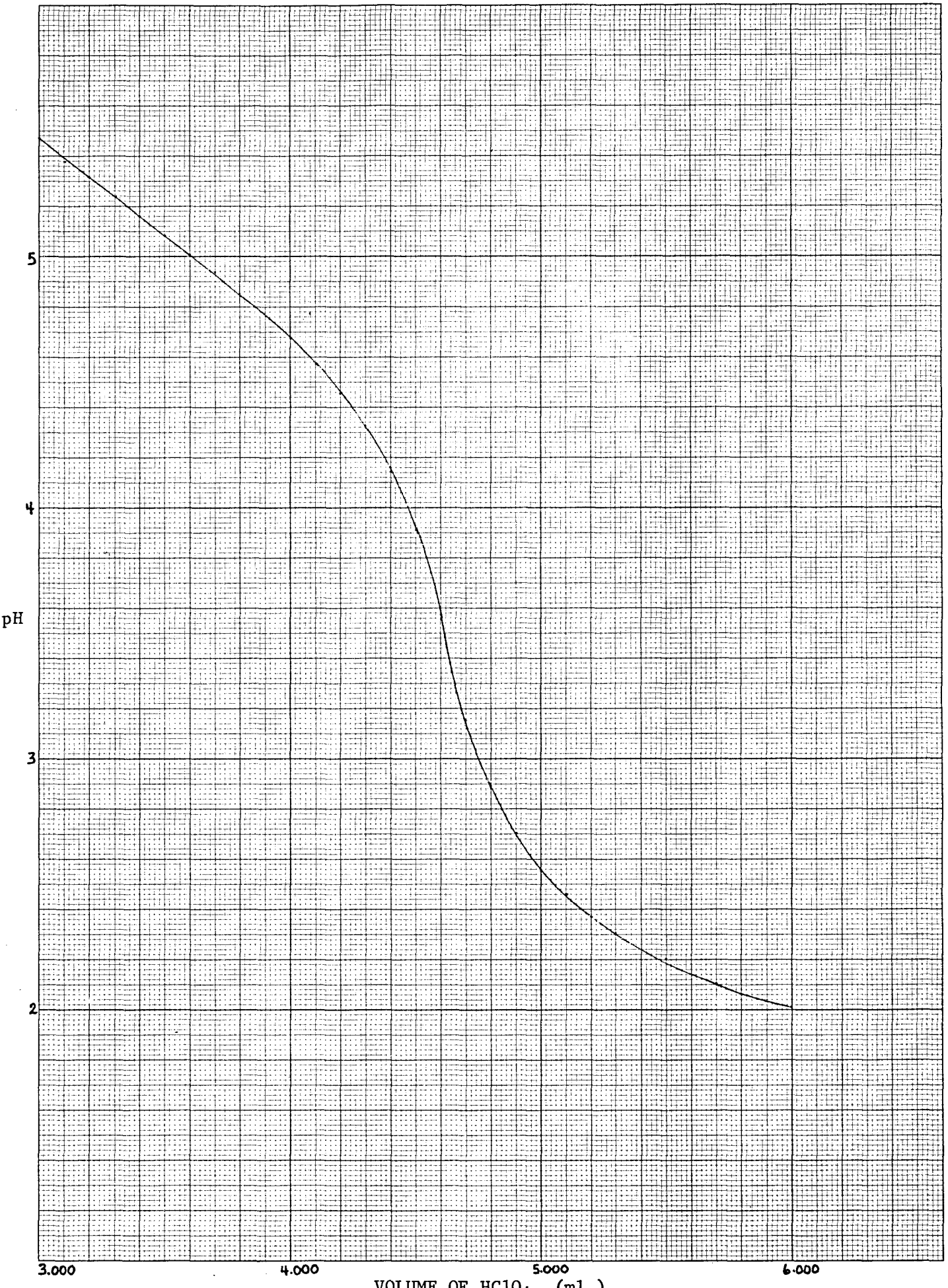
TITRATION WITH $HClO_4$ (0.1378 M)

milliliters of $HClO_4$ added	pH I	pH II	pH III
0.0000	8.7830	8.7830	8.7830
0.1000	8.4438		
0.2000	8.1649		
0.3000	7.9881		
0.4000	7.8622		
0.5000	7.7420	7.7421	7.7420
0.6000	7.6383		
0.7000	7.5511		
0.9000	7.3972		
1.0000	7.3160	7.3160	7.3162
1.1000	7.2351		
1.2000	7.1678		
1.3000	7.1010		
1.4000	7.0328		
1.5000	6.9616	6.9620	6.9618
1.6000	6.8847		
1.7000	6.8100		
1.9000	6.6231		
2.0000	6.5283	6.5281	6.5281
2.1000	6.4240		
2.2000	6.3166		
2.3000	6.1947		
2.4000	6.0790		
2.5000	5.9550	5.9551	5.9550
2.6000	5.8450		
2.7000	5.7430		
2.8000	5.6496		
2.9000	5.6048		
3.0000	5.4782	5.4782	5.4779
3.0500	5.4300		
3.1000	5.3853		
3.1500	5.3485		
3.2000	5.3122		
3.2500	5.2786		
3.3000	5.2410		
3.3500	5.2021		
3.4000	5.1638		
3.4500	5.1260		
3.5000	5.0892	5.0889	5.0890
3.5500	5.0525		
3.6000	5.0100		
3.6500	4.9790		
3.7000	4.9412		

STANDARDIZATION OF DISEC (Continued)

milliliters of $HClO_4$ added	pH I	pH II	pH III
3.7500	4.8900		
3.8000	4.8530		
3.8500	4.8117		
3.9000	4.7685		
3.9500	4.7215		
4.0000	4.6736	4.6740	4.6738
4.0500	4.6220	4.6220	4.6217
4.1000	4.5740	4.5740	4.5738
4.1500	4.5218	4.5220	4.5216
4.2000	4.4595	4.4592	4.4595
4.2500	4.3993	4.3992	4.3990
4.3000	4.3260	4.3262	4.3255
4.3500	4.2371	4.2370	4.2370
4.4000	4.1420	4.1422	4.1425
4.4500	4.0470	4.0474	4.0467
4.5000	3.9170	3.9169	3.9172
4.5500	3.7680	3.7676	3.7880
4.6000	3.5772	3.5774	3.5770
4.6500	3.3641	3.3644	3.3640
4.7000	3.1570	3.1572	3.1570
4.7500	3.0100	3.0998	3.0996
4.0000	2.8993	2.8990	2.8990
4.8500	2.7838	2.7837	2.7836
4.9000	2.7085	2.7080	2.7086
5.0000	2.5558	2.5555	2.5550
5.1000	2.4630	2.4631	2.4632
5.2000	2.3755	2.3752	2.3755
5.3000	2.3096	2.3092	2.3097
5.5000	2.2031	2.2030	2.2033
5.7000	2.1158	2.1158	2.1160
6.0000	2.0120	2.0121	2.0115

TITRATION OF "DISEC"

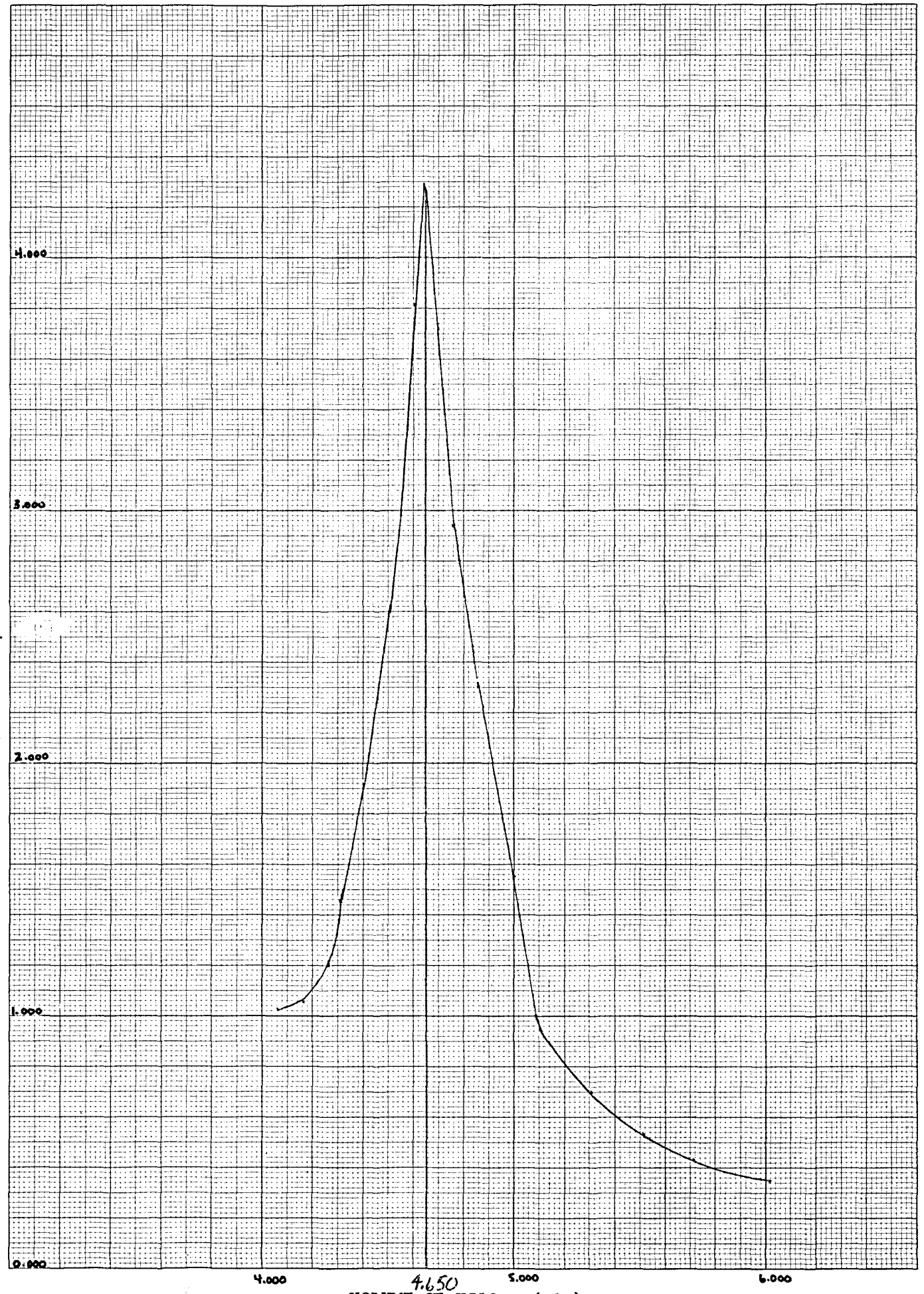


STANDARDIZATION OF DISEC

TITRATION WITH $HClO_4$ (0.1378 M)

Δ pH	Δ V	V	Δ pH/Δ V
.0516	.050	4.05	1.032
.0532	.050	4.15	1.064
.0602	.050	4.25	1.204
.0733	.050	4.30	1.466
.0889	.050	4.35	1.778
.0951	.050	4.40	1.902
.1300	.050	4.50	2.600
.1490	.050	4.55	2.980
.1908	.050	4.60	3.816
.2131	.050	4.65	4.262
.1470	.050	4.75	2.940
.1155	.050	4.85	2.310
.1527	.100	5.00	1.527
.0928	.100	5.10	0.928
.0659	.100	5.30	0.659
.1065	.200	5.50	0.533
.0873	.200	5.70	0.437
.1038	.300	6.00	0.346

TITRATION OF "DISEC"



DISEC·2$HClO_4$ STOCK SOLUTION

500 ml. of "Disec" was titrated to pH = 3.3641 (pH at equivalent point) with stock $HClO_4$ (0.1378 N).

DATA

Volume of Disec = 500 ml.
Normality of Disec = 0.01282 N
Volume of $HClO_4$ = 48.750 ml.
Total volume of solution = 548.75 ml.

Number equivalents of Disec used = N x V

= 0.01282N x 0.500 l.

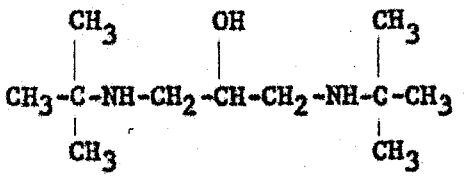
= 0.00641 equiv.

Concentration of Disec·2$HClO_4$ = $\frac{\text{no. equiv.}}{\text{Total Vol.}} \times 1000$

= $\frac{0.00641 \text{ equiv.} \times 1000}{0.54875 \text{ l.}}$

= 0.00584 M (0.01168 N)

"SYMAMINOL" STOCK SOLUTION



(M.W. = 202.343g)

Approximately 4.5 grams of Symaminol·2HCl* (M.W. = 275.28g) was dissolved in 500 ml. of CO_2-free distilled water. The solution was then passed through an Amberlite column (IRA-400, Cl type converted to OH form). The resulting solution was tested by addition of $AgNO_3$ solution. No chloride ion was found to be present.

The "Symaminol" free-base solution was titrated with standardized $HClO_4$ to determine its concentration.

DATA

50 ml. aliquots used

$$\text{Concentration of "Symaminol"} = \frac{\text{Vol. of } HClO_4 \times \text{Normality of } HClO_4}{\text{Volume of "Symaminol"}}$$

$$= \frac{3.2000 \text{ ml.} \times 0.1378 \text{ N}}{50 \text{ ml.}}$$

$$= 0.008819 \text{ N} \quad (0.004410 \text{ M})$$

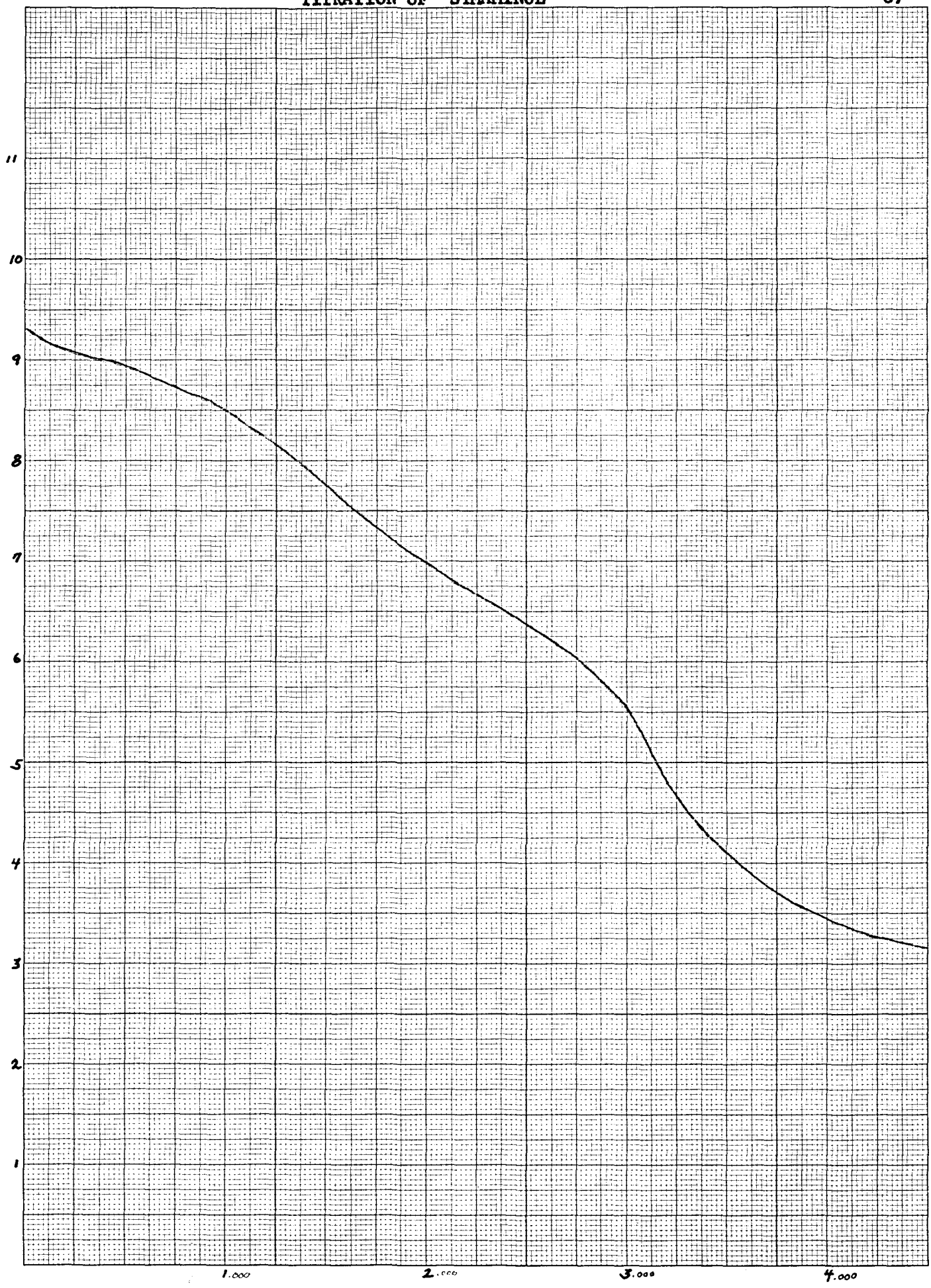
*Preparation of Symaminol·2HCl is given on page 72.

STANDARDIZATION OF SYMAMINOL

TITRATION WITH $HClO_4$ (0.1378 M)

milliliters of $HClO_4$ added	pH I	pH II	pH III
0.0000	9.2460	9.2460	9.2460
0.0500	9.2120		
0.1000	9.1823		
0.1500	9.1505		
0.2000	9.1207		
0.3000	9.0581		
0.4000	8.9970		
0.5000	8.9282	8.9300	8.9306
0.6000	8.8590		
0.7000	8.7810		
0.8000	8.6980		
0.9000	8.6125		
1.0000	8.5101	8.5095	8.5100
1.1000	8.4400		
1.2000	8.2795		
1.3000	8.1337		
1.4000	7.9670		
1.5000	7.7857	7.7850	7.7846
1.6000	7.5842		
1.7000	7.4275		
1.8000	7.2645		
1.9000	7.1245		
2.0000	6.9980	6.9995	6.9989
2.1000	6.8844		
2.2000	6.7630		
2.3000	6.6478		
2.4000	6.5335		
2.5000	6.4184	6.4175	6.4180
2.6000	6.2940	6.2932	6.2943
2.7000	6.1400	6.1420	6.1415
2.8000	6.0085	6.0100	6.0090
2.9000	5.8040	5.8050	5.8057
3.0000	5.5600	5.5995	5.5600
3.1000	5.2555	5.2563	5.2550
3.2000	4.8890	4.8900	4.8875
3.3000	4.5940	4.5961	4.5953
3.5000	4.1540	4.1525	4.1535
3.6000	3.9860	3.9845	3.9860
3.7000	3.8575	3.8571	3.8560
3.8000	3.7395	3.7400	3.7410
4.0000	3.5325	3.5310	3.5329
4.2500	3.3470		
4.5000	3.1940	3.1925	3.1945

TITRATION OF "SYMAMINOL"

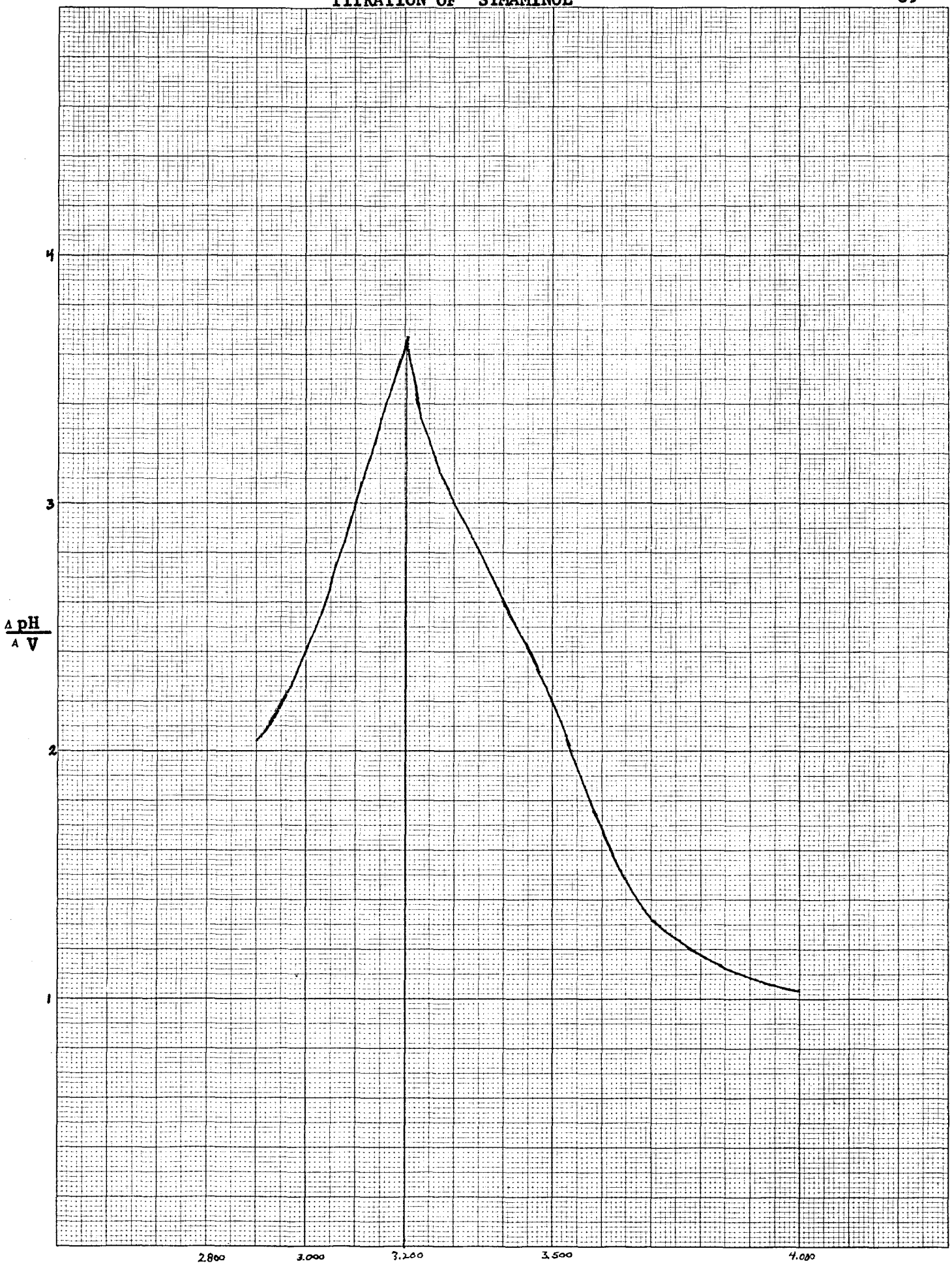


STANDARDIZATION OF SYMAMINOL

TITRATION OF SYMAMINOL WITH $HClO_4$ (0.1378 M)

Δ pH	Δ V	V	Δ pH/Δ V
0.2045	0.1000	2.9000	2.045
0.2440	0.1000	3.0000	2.440
0.3045	0.1000	3.1000	3.045
0.3665	0.1000	3.2000	3.665
0.2950	0.1000	3.3000	2.950
0.4400	0.2000	3.5000	2.200
0.1680	0.1000	3.6000	1.680
0.1285	0.1000	3.7000	1.285
0.1180	0.1000	3.8000	1.180
0.2070	0.2000	4.0000	1.035

TITRATION OF "SYMAMINOL"



SYMAMINOL·2$HClO_4$ STOCK SOLUTION

450 ml. of "Symaminol" was titrated to pH = 4.8890 (pH at equivalent point) with stock $HClO_4$ (0.01378M and 0.1378M).

DATA

Volume of Symaminol = 450 ml.
Normality of Symaminol = 0.008819 N
Volume of $HClO_4$ = (0.01378 N) = 30.000 ml.
(0.1378 N) = 25.80 ml.
Total volume of solution = 505.80 ml.

Number of equivalents of Symaminol used = N x V

= 0.008819 x 0.450 l.

= 0.003969 equiv.

Concentration of Symaminol·2$HClO_4$ = $\frac{\text{no. equiv. x 1000}}{\text{Total Vol.}}$

= $\frac{\text{0.003969 equiv. x 1000}}{\text{0.50580 l.}}$

= 0.007847 N (0.003924 M)

E. SUMMARY OF REAGENT CONCENTRATIONS

$Cu(NO_3)_2$	- Stock Solution A	0.1036 M
$Cu(NO_3)_2$	- Stock Solution B (Stock Solution A diluted 10:1)	0.01036 M
NaOH	- Stock Solution	0.1031 M
$HClO_4$	- Stock Solution	0.1378 M
$NaClO_4$	- Stock Solution	2.000 M
Disec	- Stock Solution	0.00641 M (0.01282 N)
Disec·$2HClO_4$	- Stock Solution	0.005840 M (0.01168 N)
Symaminol	- Stock Solution	0.004410 M (0.008819 N)
Symaminol·$2HClO_4$	- Stock Solution	0.003924 M (0.007847 N)

F. PREPARATION OF SOLUTIONS FOR TITRATION (METAL : LIGAND RATIO)

"Disec"

Total Volume = 100 ml. of Solution

DISEC (0:1)	CONCENTRATION OF STOCK SOLUTION	VOLUME USED	FINAL CONCENTRATION
Disec·$2HClO_4$	0.00584 M	17.1278 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
DISEC (0.2:1)			
Disec·$2HClO_4$	0.00584 M	17.1278 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock B)	0.01036 M	1.9298 ml.	0.2×10^{-3} M
DISEC (0.5:1)			
Disec·$2HClO_4$	0.00584 M	17.1278 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock B)	0.01036 M	4.8244 ml.	0.5×10^{-3} M
DISEC (1:1)			
Disec·$2HClO_4$	0.00584 M	17.1278 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock B)	0.01036 M	9.6488 ml.	1×10^{-3} M
DISEC (10:1)			
Disec·$2HClO_4$	0.00584 M	17.1278 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock A)	0.1036 M	9.6488 ml.	10×10^{-3} M

(METAL : LIGAND RATIO)
"Symaminol"
Total Volume = 100 ml. of Solution

SYMAMINOL (0:1)	CONCENTRATION OF STOCK SOLUTION	VOLUME USED	FINAL CONCENTRATION
$Symaminol \cdot 2HClO_4$	0.003924 M	25.4870 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
SYMAMINOL (0.2:1)			
$Symaminol \cdot 2HClO_4$	0.003924 M	25.4870 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock B)	0.01036 M	1.9298 ml.	0.2×10^{-3} M
SYMAMINOL (0.5:1)			
$Symaminol \cdot 2HClO_4$	0.003924 M	25.4870 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock B)	0.01036 M	4.8244 ml.	0.5×10^{-3} M
SYMAMINOL (1:1)			
$Symaminol \cdot 2HClO_4$	0.003924 M	25.4870 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock B)	0.01036 M	9.6488 ml.	1×10^{-3} M
SYMAMINOL (10:1)			
$Symaminol \cdot 2HClO_4$	0.003924 M	25.4870 ml.	1×10^{-3} M
$NaClO_4$	2.0000 M	25.000 ml.	0.5 M
$Cu(NO_3)_2$ (Stock A)	0.1036 M	9.6488 ml.	10×10^{-3} M

G. FORTRAN PROGRAM (IBM 1620 AND 407)

PART I

PROGRAM FOR CALCULATING g, pZ, AND Z FROM V AND pH

```
 1 PRINT 15
15 FORMAT (20HIDENTIFY CALCULATION)
   ACCEPT 14
14 FORMAT (49H
   PUNCH 14
31 READ 10, XM,XZ,AN,WK,AK,BK,NR
10 FORMAT (F10.8,F10.8,F8.6,E12.5,F12.5,E12.5,I3)
   PUNCH  10, XM, XZ, AN, WK, AK, BK, NR
   DO 30 J = 1, 20 , 1
 2 READ 11, V, PH
11 FORMAT (F10.7,10X,F10.7)
20 AH = 0.
   BETA = 0.
   TZ = 0.
   Z = 0.
   ALPHA = 0.
   BA = 0.
   TM = 0.
   G = 0.
   PZ = 0.
   AH = 1./(10.**PH)
   BETA = AH*AK + 2.*(AH**2)*BK
   TZ = (XZ)*(100./(100. + V))
   Z = ((2.*TZ) -((V*AN)/(100.+V)) - (AH) + ((WK)/(AH)))/BETA
   ALPHA = 1. + AH*AK + (AH**2)*BK
   BZ = (TZ) - (ALPHA)*(Z)
   TM = (XM)*(100./(100. + V))
   G = (BZ)/(TM)
   PZ = - 2.30259*(LOG (Z))
30 PUNCH 12, NR, G, PZ, Z, V, PH
12 FORMAT (I3,3X,E12.5,3X,E12.5,3X,E12.5,3X,F7.4,3X,F7.4)
   PUNCH 17
17 FORMAT (//)
   TO TO 31
   END
```

PART II

PROGRAM FOR CALCULATING K_{MZ} AND K_{MZ_2} FROM g AND Z

```
 1 PRINT 15
15 FORMAT (20HIDENTIFY CALCULATION)
   ACCEPT 14
14 FORMAT (49H
   PUNCH 14
 2 READ 10, GA, ZA, GB, ZB, I
10 FORMAT (E12.5,3X,E12.5,5X,E12.5,3X,E12.5,11X,I2)
   IF (I) 18, 20, 18
20 PUNCH 10, GA, ZA, GB, ZB
   UA = GA
   UB = (GA - 2.)*ZA**2
   UC = (1. - GA)*ZA
   UM = GB
   UN = (GB - 2.)*ZB**2
   UP = (1. - GB)*ZB
   BASE = UA*UN - UB*UM
   AX = (UC*UN -UB*UP)/BASE
   AK = 1./AX
   CK = (UA*UP - UC*UM)/BASE
   PUNCH 12, AK, CK
12 FORMAT (E12.5,10X,E12.5)
   GO TO 2
18 PUNCH 17
17 FORMAT (//)
   GO TO 1
   END
```

PART III

PROGRAM FOR CALCULATION OF HYDROGEN CONCENTRATION AND STABILITY CONSTANTS FROM VOLUME AND pH

```
   DIMENSION V(99),AH(99),G(99)
 1 READ 2,I,AN,Z,WK,NUM
 2 FORMAT (I3,7X,F11.8,9X,F11.8,9X,E14.7,3X,I5)
   PRINT 2,I,AN,Z,WK,NUM
   PUNCH 2, I,AN,Z,WK,NUM
   PUNCH 14
   DO 3 J=1,I
   READ 4,V(J),PH
 4 FORMAT (F10.0,10X,F10.0)
   PJ=15.0-PH
   AH(J)=10.0**PJ*10.0**(-15)
   G(J)=2.-V(J)*AN/(Z*100.)+(WK-AH(J)**2)/(AH(J)*Z*100./(100.+V(J)))
 3 PUNCH 12, J,G(J),AH(J),V(J)
   PUNCH 13
   DO 5 K=1,I
   UM=AH(K)*(G(K)-1.)
   UN=AH(K)**2*(G(K)-2.)
   DO 5 L=1,I
   IF (K-L) 5,5,11
11 UA=AH(L)*(G(L)-1.)
   UB=AH(L)**2*(G(L)-2.)
   BASE=UA*UN-UB*UM
   IF  (BASE) 7,8,7
 7 AK=(-G(L)*UN+G(K)*UB)/BASE
   BK=(UA*(-G(K))+G(L)*UM)/BASE
   IF (AK) 9,10,9
 9 CK=BK/AK
   GO TO 6
 8 PRINT 22,K,L
   GO TO 5
10 PRINT 23,K,L
   CK=9.9999999E98
23 FORMAT (17HAK = 0 FOR POINTS,I3,2H +,I3)
 6 PUNCH 15,L,K,AK,BK,CK
 5 CONTINUE
   PRINT 13
   PRINT 35,NUM
   PAUSE
   GO TO 1
77 STOP
   GO TO 77
35 FORMAT (10HEND OF NO.,15)
```

```
22 FORMAT (6HPOINTS,I3,2H +,I3,18HARE INDETERMINATE.)
12 FORMAT(5HPOINT,I3,1X,4HG = ,E14.7,1X,4HH = ,E14.7,1X,4HV = ,E14.7)
13 FORMAT (///)
14 FORMAT (/)
15 FORMAT (6HPOINTS,I3,2H +,I3,4H KA=,E14.7,4H KB=,E14.7,3HKC=,E14.7)
   END
```